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**Nuclear Waste Management
Semiannual Progress Report
April 1983 Through
September 1983**

**J. L. McElroy
J. A. Powell**

January 1984

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**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
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NUCLEAR WASTE MANAGEMENT
SEMIANNUAL PROGRESS REPORT
APRIL 1983 THROUGH SEPTEMBER 1983

Compiled by
J. L. McElroy and J. A. Powell
Nuclear Waste Technology Program

January 1984

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

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1.0 WASTE STABILIZATION

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1.1 HANFORD WASTE VITRIFICATION PROGRAM
(AR-05-10-02 - 80602)

The objective of the Hanford Waste Vitrification Program (HWVP) is to apply vitrification technology to a selected Hanford waste stream(s), developing a process and equipment to be utilized in a Hanford waste facility.

Summary

Program activities performed during the third and fourth quarters of FY 1983 include vitrification process development and remote equipment component development and design. Preconceptual design studies of a vitrification system were completed.

Vitrification process development included studies of glass-production rates and decay heat for waste stream options; evaluation of canister size limitation criteria; preliminary shielding calculations for the melter and canister; temperature measurements of the glass and canister, utilizing three separate scenarios; formulation of a preliminary current acid waste (CAW) glass composition; successful alteration of CAW slurry settle-out and flowability; investigation on neutralized current acid waste (NCAW) glass foaming during melter opera-

tion; and completion of a 5-day pilot-scale ceramic melter experiment.

Activities to test and remotize equipment included the completion of high-bay extension (HBE) modifications, except shake-down of remote radiocontrol and television system; installation of the turntable superstructure; major emphasis on contaminating and testing decontamination methods on test specimens; canister-related tasks, including a study of inertial welding, set-up of a canister weighing device, and level detection device; melter-related tasks, including design of an overflow discharge insert, fabrication of a discharge section mockup, additional reference lid design, and discharge electrical services evaluation; an evaluation of instrument connectors; design of a product-sampling device; and preliminary design of a melter electrode power bus.

Process Development

Candidate waste streams for the B Plant Immobilization Pilot Plant (BIPP) have included current acid waste (CAW) and neutralized B Plant acid waste (NBAW). During preliminary studies, a number of conceivable options were evaluated prior to the reference selection. Required glass production

rates and decay heat for various waste stream options were estimated to evaluate the impact on melter design and canister size selection. The waste stream options considered were CAW, NBAW, and neutralized low-sulfate current acid waste (NLSCAW) for both the 6% and 12% ^{240}Pu N-Reactor fuel at 180-day and 1-year cooling. NLSCAW is the waste generated by neutralizing the CAW generated from the PUREX flowsheet. This is a different waste, however, than the washed NCAW used as the reference feed in the B Plant process efforts, as ferrous sulfamate is not used as a reductant in this flow-sheet. Table 1.1 details the oxide loading, heat load, and glass-production rate for the various cases. This information was used to generate limitations on the waste canister and/or the glass melter.

Canister Size Limitations

The size of the canister must meet several criteria. First, the centerline temperature of the glass should not exceed 500°C during expected handling/shipping

activities. This is a conservative design value that was selected to be sure that the glass is not subject to significant thermal degradation during the predisposal period. Second, the proposed guideline in RHO-BW-CR-136/AESD-TME-3142, Waste Package Conceptual Designs for a Nuclear Repository in Basalt, October 1982, limits decay heat in the canister to less than 0.75 kW per meter of canister length at the time of disposal in basalt. Finally, the minimum canister diameter should be not less than 12 in. to meet other operating requirements.

The maximum sizes for canisters containing waste glasses with different decay heat levels are shown in Figure 1.1. These different curves show the limits for canisters with and without fins and in air or water storage. Curve 1, for air storage of canisters with no internal fins, is used to determine the maximum canister sizes for the various waste options (Table 1.2). The second column in Table 1.2 shows the total number of canisters produced per year assuming that the BIPP processes the waste from 1000 metric tons of fuel per year. The 6%

TABLE 1.1. BIPP Waste-Stream Options

	12% ^{240}Pu CAW	12% ^{240}Pu NBAW	12% ^{240}Pu NLSCAW	6% ^{240}Pu CAW	6% ^{240}Pu NBAW	6% ^{240}Pu NLSCAW
Kg Waste Oxides/MTU	40	26	130	38	20	130
Decay Heat, W/MTU						
180 day cooled	3830	3550	3830	2290	2120	2290
1 yr cooled	1460	1330	1460	656	604	656
Kg Glass/MTU (25 wt% loading)	160	100	600 ^(a)	150	80	600 ^(a)
Decay Heat, W/L glass						
180 day cooled	67	99	18	43	74	11
1 yr cooled	26	37	6.8	12	21	3.1

(a) Waste loading limited to 21.8 wt% by high Na_2O content of waste (16 wt% Na_2O limit assumed for glass).

FIGURE 1.1. Canister Size Limits

TABLE 1.2. Approximate Canister Sizes and Quantities

Waste	Canister Dia, in. (a)	Canisters per Year, 1000 MTU/yr
12% NAW 0.5 yr	8	400
12% CAW 0.5 yr	10	385
6% NBAW 0.5 yr	10	255
6% CAW 0.5 yr	12	270
12% NBAW 1.0 yr	12	180
12% CAW 1.0 yr	16	160
6% NBAW 1.0 yr	16	110
6% CAW 1.0 yr	24	70

(a) Based on a centerline maximum temperature of 500°C in air.

and 12% CAW wastes at 0.5 yr would require a canister less than the 12 in. minimum. These wastes would require aging, dilution, or canisters smaller than 12 in. before they could be vitrified.

Glass Melter Limitations

In a glass melter, the decay heat contributes part of the energy needed to keep the glass molten during idling and to evap-

orate the liquid waste during processing. The balance of the required energy comes from joule heating. The total amount of energy required by a melter is a function of melter size, melter-cavity geometry, wall thickness, and cooling losses. A correlation between power requirements and melter size is shown in Figure 1.2. The idling power from existing PNL and SRL melters is normalized to glass volume and plotted against the glass surface area available for processing. The 100% line is the total power required for idling. The 75% line shows maximum percentage of total power that should come from decay heat so a margin is available for proper control of the melter. The proposed surface area for the BIPP melter is 1.7 m² so the allowable decay heat ranges from 33 to 50 W/L, depending on the melter design. The six wastes with the highest decay heats are listed along the vertical axis to illustrate which wastes can

FIGURE 1.2. Power/Melter Correlation

be handled by the existing melter design. The high-decay-heat wastes (60 W/L) can be handled by aging the waste, decreasing the glass waste loading, reducing throughput or using a smaller melter, or making a radical design change in the melter (e.g., shallow glass cavity, forced cooling of walls, etc.). The other wastes can all be handled by the reference melter. These options are listed in order of decreasing desirability. Aging and dilution would have no effect on equipment design, although operational requirements, such as total processing rate, may have to be changed. The ultimate design and system capacity will depend on the waste stream selected and on prior cooling of the waste before vitrification.

Shielding Source Terms

Preliminary shielding calculations for the melter and the canister were completed to provide input for specifications of the cell wall thickness.

The HLW information was based on the NBAW flowsheet, which assumes 25 wt% waste loading in the glass. Shielding calculations for HLW canisters filled with CAW and NBAW glass confirmed NBAW gives the highest dose rate at the 6-month decay period. At decay periods of several years, the CAW dose rate will probably be the higher of the two.

The refractories of the melter and the stainless steel shell provide significant shielding to the sides and bottom of the melter. A simplified model of the melter was used in the shielding calculations. This model was also used to estimate the weight of the melter, 26,000 kg, including glass 18 in. deep in the cavity. Actual

weight will be slightly higher to reflect the addition of process nozzles and support members.

Shielding calculations were completed for the simplified melter and for another having very similar dimensions. A typical 12-in. dia HLW canister was also modeled for the dose calculations. Two codes were used, ISOSHLD and ANISN. The ISOSHLD takes the input isotope activities and creates an energy-dependent gamma photon spectrum; ISOSHLD can model simple three-dimensional shapes easily. ANISN has a more accurate calculational model for shielding physics but is limited by geometry constraints. For the HLW canister, ISOSHLD predicts a midplane dose rate of 13.7×10^5 rad/hr while ANISN predicts 9.0×10^5 rad/hr. Since ANISN accurately models this simple geometry, the difference is an indication of the conservatism gained by using ISOSHLD for the more complex geometry of melters and cells. (This code is being used for the cell-wall shielding calculations). The ISOSHLD dose calculations for the melter predict a dose rate of 146 rad/hr for the front face of the melter (long side opposite the discharge end). Shielding calculations for the dose emanating upward through the lid of the melter are about 10^5 rad/hr. One foot of concrete would attenuate lid dose rate down to 800 rad/hr, and 2 feet of concrete would reduce it to 9 rad/hr.

Waste Form Development

A preliminary CAW glass composition (Table 1.3) was formulated based on frit 82-10, developed for NCAW waste. The resulting glass, CAW-83-1, was found to have

TABLE 1.3. Composition of CAW 83-1 Working Glass, wt%

Oxide	Frit 82-10	Glass CAW-83-1
SiO ₂	61.7	46.3
B ₂ O ₃	15.1	11.3
Na ₂ O	14.7	11.0
Li ₂ O	7.4	5.6
MgO	1.1	0.8
Waste	--	25.0
	100.0	100.0

good leaching behavior, tolerable devitrification performance, and acceptable viscosity for the limited purposes of a working glass.

Devitrification tests used two heat treatments, an isothermal anneal for 4 days at 750°C, and a slow cooling schedule designed to mimic canister centerline thermal history. The results were qualitatively analyzed by comparing x-ray diffraction patterns with those from 76-68, a commercial HLW glass, cooled under the same conditions. Based on integrated peak intensities, CAW-83-1 annealed at 750°C has roughly the same amount or slightly more crystallinity than 76-68. The major phase in the slow-

cooled sample appeared to be nepheline, sodium-alumino-silicate.

The viscosity, 70 poise at 1150°C, is very close to Savannah River Plant and German operating viscosities.

MCC-1 leach tests were performed in both deionized water and buffered pH3 solution at 7 and 28 days. The results for silicon and the most soluble elements are compared to those for West Valley and commercial waste glasses WNZ-10 and MCC-76-68 in Table 1.4. Comparison of columns one with two and three with four shows that the leaching performance does not deteriorate down to pH3. Comparison of columns two and four shows an interesting trend developing with time; at 7 days, these five elements have been released in equal amounts, whereas by 28 days, sodium and boron releases are higher than those for silicon and lithium. Furthermore, between 7 and 28 days the molybdenum concentration in solution has decreased. These results indicate fairly rapid formation of alteration phases which affect elemental solubilities. Comparison of the last three columns shows that the CAW glass leaches somewhat more slowly than last year's WNZ-10 glass and much more slowly than MCC 76-68.

TABLE 1.4. Leaching Results for CAW 83-1 Compared to WNZ-10 and MCC 76-68

Element	Normalized Elemental Release, g/m ²					
	CAW 83-1				WNZ-10	MCC 76-68
	7 d, pH3	7 d, DIW	28 d, pH3	28 d, DIW	28 d, DIW	28 d, DIW
Si	5.2	5.0	7.2	8.0	13	26
Na	6.6	5.1	17	14	16	36
B	6.4	5.0	12	10	14	40
Li	6.5	5.0	8.3	7.0	16	NA
Mo	4.7	5.4	1.8	2.5	13	41

Conditions: MCC-1 test, 90°C, SA/V = 10 m⁻¹

Notice also that the last two glasses do not seem to form alteration phases involving the elements shown by 28 days. For instance, WNZ-10's molybdenum release is still identical to its silicon release at 28 days.

Feed Chemistry and Rheology

Samples of CAW slurry prepared in the laboratory have consistently behaved poorly when left unagitated. The solids within the slurry settle out within minutes and form a hard, nonresuspendable sediment when glass frit is used as the glass former. The sediment formed after only a few minutes was usually so difficult to resuspend (or even remove) that the glassware containing the samples could not be cleaned and were instead discarded. When raw-chemical glass formers were used rather than frit, the sediment formed was moderately resuspendable, probably due in part to frit's greater particle asperity (roughness). This asperity allows frits to pack and interlock more tightly than do raw chemical glass formers.

The implication of nonresuspendable sediment to process operation is clear. In a temporary shutdown of the melter feed system, frit or SiO_2 particles will begin to settle in process lines and equipment due to loss of turbulence. In a worst-case scenario, the suspended particles could settle long enough to prevent resuspension by resumption of fluid motion. Also, during feed system operation, such a slurry would tend to clog nonturbulent "dead spots" like T-connections and valve cavities.

Three methods have been successfully employed in the lab to alter the settle-out and flowability of the CAW slurry:

1. The addition of polyelectrolytes (polymer) in 1000 to 2000 ppm concentration of slurry samples. (The viability of polymeric additives for use in radioactive environments has not yet been evaluated.)
2. Substitution of raw chemical SiO_2 constituent with prepared 30% SiO_2 suspension having a particle size of ~10 micron (1/10 the particle size of raw chemical SiO_2).
3. Alteration of HNO_3 content within CAW slurry samples.

Polyelectrolytes were found to expand the volume of the sediment and to make the sediment resuspendable, even after days without agitation. The best performer, DOW NP-10 polymer, was found to maintain ~97% of the raw chemical glass formers in suspension virtually indefinitely, and thus prevent all but ~3% of the particles from settling out. In addition, the suspension remained fluid.

A CAW slurry sample was prepared using the ~10 micron SiO_2 suspension (du Pont Ludox SM) and allowed to stand, unagitated, for two days. No particle settle-out was observed and the resulting suspension remained fluid.

It was found that excess nitric acid does not prevent particle settle-out, but that it does cause the resulting sediment to be easily resuspendable. However, since an increase in HNO_3 concentration (from 1.06M to 1.35M) would adversely affect other processing aspects, this approach is not considered viable.

Glass Foam Control

Glass melter operation with NCAW glass indicated that glass foaming could be a potentially significant operating problem. An investigation into cause and control of

foaming was initiated. Glass samples from various defense waste processing programs were analyzed to maximize the number of data points.

Results of a new laboratory technique to measure the foaming tendency of glass melts were successfully correlated with observations of foaming from melter trials of HWVP and WV glasses and from earlier trials with Savannah River (SR) compositions. Of these, SR glasses made from liquid feed and WV glasses made from calcined feed showed the least tendency to foam in the lab test. Little or no foaming was observed in their melter runs. The foam was less suitable in the lab test of the SR glasses, possibly due to their lower viscosity. HWVP and WV glasses from melter trials plagued by foaming tended to foam much more in the lab test, with perhaps multiple types of foam and considerable day-to-day variability. The tendency to foam is much greater in HWVP and WV glasses than reported for commercial soda-lime and borosilicate glasses. Analytical results suggest that redox reactions involving iron, cerium and chromium appear to have no major role in generating foam.

Following are the primary conclusions from the study:

1. Oxygen is the dominant gas in the foam collected from the melter.
2. Evidence linking redox reactions and foaming is weak because:
 - a. Iron occurs only in the ferric state in HWVP and WV glasses and foams sampled from the melter, indicating that measurable changes in iron redox that produce ferrous iron and liberate oxygen have not occurred. The absence of ferrous iron is attributed to mutual redox interactions among iron, cerium and chromium.
 - b. Multivalent ions other than iron (cerium, chromium) are in a greater state of oxidation in the glass foam than in the glass, indicating that they are recipients rather than producers of oxygen.
3. A laboratory method to evaluate foaming tendency in glass samples has been developed. It measures the reduced pressure, under isothermal conditions, at which bubbling occurs due to gaseous supersaturation in the glass melt. Glasses that have lower bubbling (reboil) pressures are considered to be less prone to foam in the melter. Preliminary results indicate:
 - a. Glasses sampled from melter trials characterized by numerous foaming episodes reboil at considerably higher pressures than glasses from trials having little or no foaming.
 - b. Some glasses from each melter trial having foaming problems generated a layer of foam in the crucible at 1 atm before the test temperature was reached, in addition to the bulk reboil detected later at reduced pressures. This could suggest the presence of multiple glassy phases. Glasses from melter trials with few foaming episodes did not develop this initial foam layer in the crucible.
 - c. Considerable variation exists among samples collected from the same melter trial at different times. This could suggest mixing problems in the melter or inhomogeneous feed.
 - d. Savannah River (SR) compositions using the current glass-forming frit and formic acid in the liquid feed collected from melter runs had lower reboil pressures than any HWVP or WV

glass made by liquid feeding. These melter runs had few foaming events. Foam did not rise in the test crucible for the SR glasses at the reboil pressure, unlike the HWVP and WV glasses, suggesting that their foam is less stable. The reason for this is unclear, but may be due to their lower viscosity.

- e. Compositionally simplified lab melts made with reagent grade oxides have significantly lower reboil pressures than the analogous HWVP and WV glasses made by liquid feeding in the PSCM. However, the WV lab melt and melter glass made with a calcined feed have similar reboil pressures. This could suggest that dissolved water in the glass and foaming are related, as has been reported in the literature.
 - f. All HWVP, WV and SR melter glasses tested have reboil pressures several times greater than those characteristic of commercial soda-lime and borosilicate glasses, and are, thus, much more prone to foam.
4. Although not proven at this point, reducing viscosity to destabilize foam may be an attractive approach.

Pilot-Scale Melter Studies

A 5-day pilot-scale ceramic melter experiment was completed. During the 112-hr test ~2300 L (~3130 kg) of a simulated CAW and glass former slurry were fed to the melter, producing ~700 kg of glass product. This was the fourth liquid-fed experiment this fiscal year and the eighth test conducted by the HWVP.

The slurry composition was a nitric acid-based slurry having a nitric acid concentra-

tion of ~1.1 moles/L and an oxide loading of ~300 g/L. The primary objective of the experiment was to evaluate the feed's processability. This included determination of a maximum stable feed rate, glass-melt foaming tendency, cold-cap stability and venting, off-gas surges, particulate entrainment, and feed-system upsets.

The melter operation was very stable, with no glass foaming evident and only minor off-gas surges. Few active vent holes (which occur as a result of cold cap venting in the lower areas of the cap adjacent to the glass melt surface) were observed. The cold cap was not overly rigid or thick. Unfortunately, this glass composition was very slow in melting, and a maximum feed rate of only ~24 L/hr was possible operating at 1150°C. This feed rate was only ~45% of the expected possible maximum. The very slow melting characteristics of the feed composition are similar to those of compositions very high in the refractory mineral elements such as silica alumina, and zirconia. These elements are very good thermal insulators and in the absence of fluxing agents melt at temperatures over 2000°C. If the cold cap was enriched in refractory elements and depleted in fluxing agents, such as sodium and boron, the heat flux from the glass to the slurry would be diminished. This would result in a lower processing rate capability, which was in fact observed. The cold-cap thickness did remain stable throughout the experiment, indicating that the melt temperatures were adequate and that fluxing agents were present. Table 1.5 summarizes the experiment.

Analysis of the feed early in the experiment showed it to be low in the prescribed amount of sodium borate and silica, both glass formers. As sodium borate is composed of fluxing agents, it was reasoned that this

TABLE 1.5. PSCM-17 Summary

Total run time	111.8 hr
Total down time ^(a)	13.3 hr
Efficiency	88%
Total feed to melter	2313 L (3131 kg)
Average feed rate ^(b)	23.4 L/hr (32.2 L/hr-m ²)
Glass produced ^(c)	694 kg

(a) 5.4 hr during feed composition adjustment
7.9 hr due to feed system.

(b) Based on actual feeding time only.

(c) Calculated on a feed-oxide loading of
300 g/L.

might be the cause of the slow melter processing rate. The feed was then adjusted with these two chemicals and operation continued. During the last 58 hr of the melter operation processing the corrected feed, no noticeable improvement in processing rate was measured. This might indicate that the glass composition itself may be the cause for the low rate.

During the last 9 hr of melter operation, the electrode power was increased to realize the average glass temperature of ~1225°C. This was done to observe any process rate improvement at the elevated temperature. Before this increase, the melter had been operated with glass temperatures between 1150 and 1180°C. At the elevated temperatures, there were no incidents of foaming and feed rates of ~26 L/hr were maintained.

High-Bay Extension (HBE) Facility Development

A mock cell wall was designed and fabricated to aid in simulating remote conditions so that component remotability in BIPP could be evaluated. Piping, wiring and instru-

mentation to support the modification of the facility were also completed.

An existing crane was modified to incorporate a rotating cell-type hook. All crane operations, including crane-held impact wrench were converted to radio-controlled operation. A closed-circuit television viewing system has been installed and is in the shakedown stage. Remote operations will be viewed through the television system to simulate cell conditions.

An operational, full-scale turntable was designed, fabricated, and installed in the HBE and is discussed below. A melter box having the same outer dimensions and remote flanges similar to the reference melter design was constructed, fabricated and installed in the HBE. Support structures were designed, fabricated, and installed for supporting the melter box and turntable at their reference cell elevations with respect to the mode cell wall, floor, and gallery.

All HBE modifications have been completed except for final shakedown of remote radio-control and television systems.

Turntable

The turntable superstructure and body has been designed, fabricated and installed in the HBE facility.

Two melter/turntable connections were designed during the report period to replace an inadequate isolation valve that had been designed and tested in the previous report period. A liquid metal-based seal concept was designed but discarded prior to fabrication in favor of an air-activated metal bellows seal concept. Tests to evaluate candidate low-melting-point metals were completed in support of the nonreference design. Fabrication of the metal bellows offsite has

proceeded more slowly than anticipated, and testing will be postponed until the bellows assembly and a bellows flange/turntable E-ring arrives from offsite. Testing will evaluate the feasibility of the bellows seal method for remote operation.

Canister Decontamination

Major emphasis during the report period was on contaminating the test specimens and testing the decontamination methods on those specimens. This included soak, spray, and leach tests with water on specimens coated with liquid simulated waste or calcined simulated waste, and selected tests on specimens contaminated with glass or volatilized cesium.

The following are major portions of this work:

- Specimens were prepared by either coating them with liquid or calcine and then exposing them to the simulated canister-filling thermal cycle or by exposing them to the thermal cycle first and subsequently applying molten glass or volatilized cesium.
- Leach tests were performed on specimens that had been coated with calcine or liquid, baked, and had the baked-on coating removed prior to immersion in the water bath.
- Water spray tests of 75, 200, 970, and 10,000 psi at both hot and cold temperatures were performed on liquid-coated or calcine-coated specimens. Glass-contaminated specimens were tested with the 970 and 10,000 psi water spray.
- The electropolishing technique was applied to liquid-coated, calcine-coated and glass-contaminated specimens.

Water soak and low-pressure sprays have been ineffective at completely removing any of the contaminants. The 970-psi spray removed 95% of the baked-on coatings but did not remove either the oxide film or the adherent glass. Electropolishing effectively removed both liquid and calcine coatings and oxide films but not the adherent glass. The 10,000-psi water removed the baked-on liquid and calcine contamination and the oxide film.

Work in progress includes tests with 10,000-psi water spray on glass-contaminated specimens; soak and spray tests using standard Citrox solution; soak and spray tests on volatilized-cesium-contaminated specimens; and surface analyses on selected specimens from the spray leach tests.

Canister Welding and Inspection

Component design studies were performed on the inertia welder, backup tungsten inert gas (TIG) welder, and the inspection system. The results were used to select the components for the reference closure system. The system selected is basically similar to one used in the preconceptual design: vertical-mounted inertia welder, swing-arm for canister positioning, and a wheel-type ultrasonic scanning device for the final weld inspection.

The results of the inertia welding study included a relatively detailed conceptual design of the machine, recommendations for several facility changes, and a description of the welder operational requirements. The study established that inertia welding is feasible and can provide the expected performance advantages over other types.

The inspection study established the feasibility of ultrasonic inspection of an inertia weld and provided a conceptual design for the inspection technique and equipment.

The study was made on the TIG welder to bring the backup welding technology to the same level as the reference process. The conclusion of the study was that the TIG process is feasible and can be applied to BIPP. However, issues such as weld reliability and ease of operations make the TIG process less attractive than the inertia process.

Canister Weighing

The strain-gauge load cell has been adapted for use as a remote canister-weighing device. The load cell will be used to weigh the contents of the canister being filled during the canister-filling operation. Remotization of the device involved design of a jumper to connect the load cell with operating gallery instrumentation and a swing-arm to transfer the canister weight (force) to the load-cell pad, located on the deck of the turntable. The load cell will provide another means of measuring the amount (mass) of product in the canister as compared to the level-detection system, which determines the product volume. Both systems comprise an important part of the process quality control. The load cell and swing-arm mechanism have been fabricated, the remote jumper is being fabricated (at J. A. Jones Company), and the gallery instrumentation has been procured.

Canister Level Detection

Design and testing of a ^{60}Co -source-mobilizing device was completed. The device consists of a source housing that is linked to an actuator shaft turned by a motor. As

the shaft is rotated, the source travels downward and is made visible, for a discrete period, to each of a series of NaI γ -ray detectors. In the proposed configuration the array of detectors is mounted in the cell wall and views the mobile ^{60}Co source through the canister being filled. The actuator shaft is designed to cycle the mobile source upward and then downward along a travel distance that corresponds to the product stream path (descending from the trough pour spout to the bottom of the canister being filled). As the interposed canister is filled, the vitrified waste product reduces the intensity of the γ -rays that pass through it from the ^{60}Co source to the detectors. This source attenuation can be detected to establish whether the canister contains glass. The vertical array of detectors allows the presence of glass to be verified at several discrete levels within the canister. With this information, the volume of glass within the canister at a given time can be calculated. Testing has verified the device's remotability and operability once installed.

Melter Overflow Discharge Insert

A remotely removable insert for the discharge melter overflow has been designed and is being fabricated for testing. The purpose of the insert is to provide a means to remove a possible glass plug that could form in the bottom of the melter discharge section. The metal insert is in the shape of an inverted cone. Testing will verify the insert's remotability and how well the material withstands operating temperatures.

Melter Discharge Thermal Mockup

A full-scale mockup of a discharge section has been fabricated and installed and is undergoing tests. It incorporates the current reference lid, trough and air-cooled melter electrical connection designs. Refractory materials are similar to those of the current reference melter design as regards heat transfer. The mockup is completely operational and contains eight heating elements suspended from the removable lid. Plate heaters located at the rear are used to simulate the heat of molten glass within a melting cavity. The heat-sink effect of glass product within a canister (located in the turntable below the trough opening) is simulated using a steam coil. The steam coil is located within a mock removable discharge insert located on the interior floor of the mockup. During testing, a nozzle on the discharge lid is connected to a building vacuum system and air is inlet at the base of the assembly through the mock insert. This flow of air simulates a hypothetical inleakage through the reference melter/turntable seal.

The testing will be to measure the temperature distribution along the trough, warpage and temperature distribution of the dam, and integrity of refractory materials. The effect on dam and trough temperature distribution of hypothetical air inleakage (through the melter turntable connection), the presence of cold product, variations in dam cooling rate and loss of lid heating elements will be measured.

Instrumentation includes over 50 type K thermocouples for temperature distribution measurement, a voltage selector panel and digital multimeter for live amperage and voltage measurement to enable the performance of the heating elements to be evaluated.

Photographs of the interior of the mock-up assembly taken between periods of operation will assist in evaluating material integrity.

Melter Discharge Section Lid

Evaluation of a previous reference lid design indicated that further design development was required to provide more protection for the heating elements during remote installation. In that design, no provisions had been made for preventing the heating elements from contacting the melter or other cell equipment during remote installation of the lid. Such contact, made while lowering the section heater, could easily damage the elements and put the discharge section out of commission.

Two methods for protecting the heaters were considered. The second (and current reference) consists of two remote dowels suspended from the periphery of the lid flange. The dowels extend lower than the heaters and thus make the initial physical contact with the melter during lid installation. The lid is aligned with the melter using the dowels; alignment is achieved while the heating elements remain safely above the surface of the melter.

The first method involved a protective shield surrounding the element assembly. The shield, attached to the underside of the lid flange, would be lowered, with the elements, into the melter discharge section. Due to concerns that the protective shield would warp during discharge section operation and cause damage to the elements, the shield design was shelved in favor of the remote dowel method.

A reference lid that incorporates the two remote dowels was fabricated as a component in the Melter Discharge Thermal Mock-Up

(described elsewhere) and will be remote tested using the HBE remote testing facility.

During the evaluation of the previous lid design, it was noted that air inleakage attributable to the discharge lid may be great enough, i.e., over 10 scfm at a vacuum of 10 in. H₂O, to present a burden to melter operation. The primary source of inleakage has been found to be the relatively low pressure drop through the porous heaters. (Leakage through the lid to melter seal was found to be negligible.) To minimize inleakage, two airtight covers have been specified and are being fabricated for testing. The covers are rectangular boxes that are seal-welded to the lid and are sized to enclose four heating elements each. The sides of the covers are air-cooled and can remove up to 8 kW each and maintain an internal temperature of ~400°C. (The cooling is required to prevent failure of the element electrical contacts at temperatures >500°C.) The electrical leads extend through air-tight fittings atop the covers. Cooling air service will be provided using conventional remote cell techniques.

Melter Discharge Electrical Services

The current reference concept is to provide separate electrical service input and output (I/O) lines to each of the eight heating elements for a total requirement of 16 through cell-wall lines. A remote 20-pin, 90 amp/pin connector is ~80% fabricated and will be evaluated as the electrical service connector. Sixteen of the 20 pins will be used. The capability to remotely connect the 16 I/O lines will result in the ability to wire and reconfigure the heating element electrical circuit(s) in the operating gallery for tighter element control. In addition, if a heating element should fail, this

remote wiring capability will enable the remaining seven heaters to be reconfigured into their optimum circuit, thus avoiding a possible "domino effect" loss of the remaining elements.

A high-temperature (400 to 550°C) electrical contacting clamp has been designed, fabricated offsite, and is currently being tested. The new clamps replace low-contact pressure clamps that have tended to fail during nonremote testing due to their poor contacting, and thus have generated high heat at the point of contact. Thus far, the clamps have been installed on the heating elements being used in the discharge thermal mockup. With the discharge section interior at 1000°C and with an amp load of 115 A, the exterior surface temperature of one of the clamps remains at a constant 400°C (in 70 to 90°C air with natural convection only). The clamps are silver-plated (0.005 in.) for extended life in a potentially corrosive environment.

Instrument Connectors

Two remotely installable multi-pin instrument connectors will be tested using the HBE facility. Testing will involve remote installation and removal, and verification of contact performance.

The reference connector contains 40 pins and was designed and prototype-tested at Savannah River Laboratory (SRL). During fabrication of the connector at PNL (80% complete) several minor revisions were made to the SRL prints. Testing will include the measurement of electrical resistances across connector pins to verify previously collected (SRL) data and remote crane-and-impact wrench installation.

The alternate connector contains fewer pins but has the advantage of being installable by crane only (no impact wrench).

Product Sampling

A design revision to the melt sampler (previously tested) that will allow the sampler to interface with the revised canister neck and canister grapple and to fit within the canister-to-turntable clearances has been developed and will be tested pending design approval. Remote demonstration will be accomplished using the HBE facility.

Melter Electrode Power Bus

A direct through-wall power bus with high ampacity (~2000 A) is being designed and will be mocked-up and tested. The power line extends from the operating gallery, through the cell wall and into the melter, where it attaches directly to an electrode. One power line (bus bars) is required for each electrode. The bus bars will tentatively be made of Inconel 690 and stainless steel type 316. The Inconel 690 will constitute the portion of the bus extending from the cell wall to the electrode, while the stainless steel will be used for the part of the bar passing through the cell wall to the operating gallery. The bar material has been sized as stated in the previous monthly report. The bus bar will be equipped with ducts through which electrode cooling air will be routed and a thermocouple access duct to the melter electrode. The electrode temperature-monitoring thermocouples will be installable from the operating gallery. The design criteria include prevention of gallery contamination and of cell-wall thermal degradation.

Testing will involve verification of ampacity using a 2000-A power system. Heat transfer will be simulated and evaluated, and thermocouple deployment from the gallery will be demonstrated.

1.2 IN SITU VITRIFICATION OF HANFORD WASTE AND TRU WASTE (AR-05-10-02 - 80441/AR-05-15-20 - 80583)

Summary

Work during this reporting period focused on three tasks: 1) completion of the pilot-scale radioactive field test; 2) completion of an economic analysis of in situ vitrification applications; and 3) completion of the public and occupational safety analysis, including a far-term (beyond institutional control) performance assessment.

To provide greater continuity and clarity for the reader, this report combines results of work in two programs. The program In Situ Vitrification of TRU Waste concluded at fiscal year end.

Pilot-Scale Radioactive Field Test

The completion of the pilot-scale radioactive field test in June 1983 met a major milestone of the in situ vitrification (ISV) program. (The previous report in this series, PNL-4250-3, describes test preparations and process equipment.)

The test vitrified a makeup site in which 25 kg of soil containing 600 nCi/g transuranic (TRU) waste simulated a highly radioactive area (or "hot spot"). The made-up source also contained mixed fission products with a total activity of 30,000 nCi/g, which exhibited a surface exposure rate of 100 R/hr before it was emplaced in the test site. Assuming that during vitrification the material

was distributed uniformly within an 8-tonne block, the resulting concentration is less than 5 nCi/g TRU waste. No radionuclides were released to the environment during the vitrification process.

Startup went smoothly. The electrical power system was operated below a total input of 600 amps, providing a safety tolerance to prevent overload of the main safety switch fuses at the substation. Total operation time was 23 hr.

The off-gas system performed well during the test. No detectable releases were recorded from the off-gas stack sampler. This provides assurance that all the radioactive material was contained within the off-gas system. The hood vacuum was maintained between 1.2 to 1.3 in. water throughout the run, except at initial contact with the plastic materials containing the radioactive material. This contact dropped the vacuum down to 0.5 in. water for about 1 hr. The pressure drop of the first-stage HEPA filter did not vary significantly: the pressure drop was about 0.8 in. water at the beginning of the run and 1.05 in. at its completion. Thus while some material reached the primary HEPA filter, it was contained there, as the pressure differential did not increase in the second-stage filter. This was corroborated by the low radiation level measured on the surface after the run: 700 disintegrations/min beta-gamma on the first-stage HEPA filter and no detectable radiation on the second-stage filter. The low pressure drop also indicates that the Hydro-Sonic scrubber effectively scrubbed the submicron particles from the off-gas stream.

The heat losses remained low for the first 8 hr into the run. A stable cold cap was initially established, apparently because of the reduced power level and the depth of the

initial startup path. Later in the run, higher heat losses as indicated by high plenum temperatures (300 to 350°C) were observed. Higher CO₂ losses were related to these higher plenum temperatures, indicating a higher oxidation rate of the graphite electrodes through the last 15 hr of the run. Off-gas system temperatures were as expected for all monitored points. The venturi ejector was the primary cooling device, eliminating most of the heat plus scrubbing the larger particles (>2 microns) from the off-gas stream. The Hydro-Sonic scrubber operated with a pressure differential of 95 in., providing very efficient scrubbing for the smaller submicron particles. The heater stabilized the HEPA inlet temperature at 60 to 65°C. No water was found in the first-stage HEPA filter, as was expected because the pressure drop across the first-stage HEPA increased by only 0.2 in. water.

The melt grew in an unusual manner on this run, apparently due to the initial depth of the startup path. A rapid depth increment was noticed at the onset of melting. The 2.5-ft centerline depth was reached ~5 hr into the run (see Figure 1.3). At that same time, however, the outer edge of the melt at the electrode centerline was only 1 ft deep. As the melting continued, the vitrification zone assumed a more standard shape as lateral growth increased and the rate of vertical growth decreased. The approximate dimensions of the block are: 5 ft deep and 9 in. horizontal growth beyond the electrode centerline (as monitored at the 3 ft depth). These dimensions indicate that a standard pilot-scale block of 5 to 6 square ft on the surface by 5 ft deep was created. The block is estimated to weigh 8.6 tonnes (19,000 lb). Using this weight together with the 6900 kWh obtained from the power depth plot in

FIGURE 1.3. Pilot-Scale Radioactive Demonstration

Figure 1.3, the estimated energy-to-mass ratio is 0.8 kWh/kg. These numbers will be confirmed later during analysis of the block itself.

The radiation level detected by instrumentation at associated points throughout the test changed as radioactive material within the melt zone was reached. Both monitors at the containment module front and back and the first-stage HEPA filter showed a slight increase of ~ 0.01 mR/hr. The radiation exposure did not increase, according to checks of the second-stage HEPA filter and control area. The hood area monitor showed the highest increase, from 0.04 to 0.07 mR/hr. The most common reading was 0.06 mR/hr, observed at the hood area after the container was reached. Surveys and smear samples from the exposed seals on the hood--including the

viewport window, electrode seals and the HEPA filter inlet flange--showed no smearable contamination. The off-gas scrub solution samples have been bagged out of the containment module and are being analyzed at PNL for radionuclide content. A survey was taken of the containment module and its contents and initial readings detected no contamination, indicating this off-gas system effectively contains contamination within the hood, the off-gas piping and associated equipment.

Post-test sampling and analysis will be completed in FY 1984. Preliminary results indicated that high decontamination factors were obtained, as shown in Table 1.6.

Economic Analysis

The cost was estimated for using ISV as an in-place stabilization technique in two types of applications, a TRU-contaminated soil site and a burial trench.

The components that contribute to the basic cost of ISV are site preparation activities, annual equipment charges, operational costs such as labor, and consumable supplies such as electricity and electrodes. Five different configurations for TRU-contaminated soil sites, employing the large-scale system, were evaluated, using the four basic cost-contributing categories. The results are provided in Table 1.7.

TABLE 1.6. Gamma-Emitting Radionuclide Inventory Losses to the Off-Gas System

	^{137}Cs	^{60}Co	^{106}Ru
Scrub solution, Ci	1.3E-4	4.0E-5	3.1E-5
Piping, Ci	7.1E-6	7.8E-7	4.3E-7
HEPA filter, Ci	5.0E-6	1.8E-7	1.1E-6
Containment hood	Analysis Ongoing		
Current DF	140	240	645
Retention in block, %	99.3%	99.6%	99.8%

TABLE 1.7. Cost Estimates for 5 ISV Large-Scale Configurations

Number	Site	Power	Heat Loss	Manpower Level	Total Cost of Soil Vitrified, 1982 \$/m ³
1	Hanford	Local	High	Average	142
2	Hanford	Local	Average	Average	116
3	Hanford	Local	Average	Above avg.	138
4	Generic	Local	Average	Average	135
5	Generic	Portable	Average	Average	179

When using Table 1.7, it is recommended that ranges be employed for making cost estimates. For example, to estimate the cost of selectively vitrifying portions (a volume of 2900 m³) of the 216-Z-1A site at Hanford, as shown in Figure 1.4, the lower boundary of the range should be case 3 (local power, above-average manpower, average heat losses): \$138/m³, for a total cost of 2900 m³ x \$138/m³, or \$400,200 or \$400 K. The upper boundary of the range should be a combination of cases 1, 2, and 3 (local power, above-average manpower, and high heat losses), which calculates to be 2900 m³ x \$138/m³ x [ratio of heat loss effects: 142 (case 1)/116 (case 2)] = \$489,900, or \$490 K.

The geometry of the site, cost of power, and soil moisture can significantly affect cost. Data were developed to illustrate the effects by determining the cost of vitrifying an entire burial trench in an eastern and western U.S. site, assuming that the geometry of the trench (Figure 1.5) was the same. Table 1.8 summarizes the results of the evaluation.

A comparison of the costs in Tables 1.7 and 1.8 shows that the effect of increased depth and changed site geometry and soil moisture is indeed significant. Here, geometry is a very important factor because the volume of waste vitrified does not equal the total volume vitrified, as it did in the pre-

vious case. Again, when using these values for planning purposes, ranges should be employed, adjusting for heat losses and manpower levels.

For comparison, the charge for disposal of low-level defense waste at Hanford is \$145/m³, and the cost of placing TRU waste in 20-year retrievable storage is \$370/m³. Estimates for exhumation, processing, certification, and emplacement at WIPP range from \$12,000 to \$25,000/m³, depending on the complexity of the site (US DOE 1980; Bishoff and Hudson 1979).

Analysis of Occupational and Public Safety

To analyze the occupational and public safety of routine and nonroutine ISV operations for both the near and far term, a Hanford waste site (the 216-Z-1A tile field in the 200 area) was selected as a reference. Radionuclide release rates from the soil during vitrification were estimated, and the 216-Z-1A waste inventory reported by Owens (1981) was the basis for the radionuclide source term.

Tables 1.9 and 1.10 give the radiation doses from routine operations in the near term for both the ISV worker and the public, respectively. The doses calculated for ISV operation at this reference site are substantially below the DOE regulations on exposure

FIGURE 1.4. Waste Distribution in a Site 90 x 4 x 4 m

Trench dimensions (L x W x D)
 Contaminated zone dimensions (L x W x D)
 Soil moisture (dry weight bases)

Hanford Site	Eastern Site
150 x 15 x 7.5 m	150 x 15 x 7.5 m
151 x 16 x 8 m	152 x 17 x 8.5 m
5%	25%

FIGURE 1.5. Characteristics of a Generic Waste Trench

TABLE 1.8. Cost Estimates for Vitrifying a Waste Trench

Parameter	West 1	West 2	East 1	East 2
Heat loss	High	Avg	High	Avg
Power	Local	Local	Local	Local
Manpower	Avg	Avg	Avg	Avg
\$/m ³ waste	276	199	506	300

TABLE 1.9. Whole Body Radiation Doses from Routine Operations

Occupational Dose (Electrode Emplacement)

All workers 0.09 man-rem

Maximum worker: 0.01 rem

Natural Background

Dose rate: 7 μ R/hr

Total (1880 hr): 0.01 rem

TABLE 1.10. Public Dose Commitments from Routine Operations (critical organ)

	Max. Exposed Indiv., rem	Population man-rem
1st yr dose (lungs)	3×10^{-8}	9×10^{-3}
50 yr dose (bone)	1×10^{-5}	5×10^{-1}

for routine operations to both workers and the general public (US DOE 1981a). Of all activities associated with ISV operations, the maximum occupational dose is expected to occur while the worker is placing electrodes. The low exposure levels are seen in Table 1.9, which shows the maximum exposed worker would receive in this activity a dose roughly the same as natural background radiation.

Abnormal exposures for both the ISV worker and the public from the vitrification process were calculated using worst-case scenarios. The most serious abnormal condition is a break in the off-gas line. For the specific exposures calculated, see Tables 1.11 and 1.12. While there are no standards for doses resulting from accidental releases, accidents that result in any individual receiving a total body dose >25 rem must be reported

immediately, and any that result in a dose >5 rem for the total body must be reported within 72 hr (US DOE 1981b). None of the public doses from potential accidents investigated for ISV application at site 216-Z-1A falls within these categories.

Far-term (beyond institutional control) exposures were calculated for transients, inadvertent intruders, intentional intruders, and permanent residents in the vicinity of the waste site. Doses were calculated for these categories for individuals 1000 and 10,000 years in the future using three scenarios: doses resulting from a site that is 1) left in its present state, 2) covered with an engineered barrier, and 3) selectively vitrified in the highly contaminated areas and covered with an engineered barrier (see Table 1.13). Pathways of concern were determined and evaluated using the allowable residual contamination level (ARCL) techniques described by Napier (1982). The pathways are direct irradiation; inhalation of resuspended material; and ingestion of contaminated crops, ground water, and animal products.

For transients the undisturbed site does not pose a direct radiation hazard at the surface because the radiation levels are at background. This is true even for the unaltered site due to the shielding properties of the soil cover. However, for permanent residents the growing of gardens and eating of the garden produce could produce an exposure of 10 rem/yr from the unaltered site for

TABLE 1.11. Occupational Doses from Accidental Releases, 120-hr Run, 15 Sets (concentrated inventory)

Accident	Number of Personnel	Length of Exposure	1st Year Dose Commitment to Each Worker, rem		
			Total Body	Bone	Lung
Uncontrolled venting	1	1 min	1×10^{-3}	2×10^{-2}	2×10
Break in off-gas line	1	5 min	6×10^{-3}	1×10^{-1}	1×10
Excess overburden removal	2	10 min	3×10^{-3}	4×10^{-2}	5×10

TABLE 1.12. Public Dose Commitments from Postulated Abnormal Occurrences

	Maximum Exposed Individual, rem	Population, man-rem
Uncontrolled venting		
1st year (lungs)	5×10^{-5}	2×10^{-1}
50 year (bone)	5×10^{-4}	2×10^0
Off-gas line break		
1st year (lungs)	3×10^{-2}	1×10^2
50 year (bone)	3×10^{-1}	1×10^3
Excessive overburden removal		
1st year (lungs)	1×10^{-2}	3×10^1
50 year (bone)	9×10^{-2}	3×10^2

TABLE 1.13. Public Dose Estimates for Far-Term Routine Scenarios, rem

Direct Irradiation	Maximum Annual Total Body Dose	
	Year 1,000	Year 10,000
Unmodified site	Background	Background
Vitrification and engineered barrier	Background	Background
Engineered barrier	Background	Background
Ingestion		
	Year 1,000	Year 10,000
Unmodified site	10	10
Vitrification and engineered barrier	0.01	0.01
Engineered barrier	0.01	0.01

both the 1000 and 10,000 year scenario. With an engineered barrier and selective vitrification, the dose would be reduced to 1×10^{-2} rem/yr, as shown in Table 1.13.

The scenarios that best distinguish the capabilities of the selectively vitrified sites from unaltered sites and barrier sites involve intentional and unintentional human intrusion (see Table 1.14). For a vitrified site, the worst case is drilling into the glass block because the relatively large quantity of respirable fines generated may result in inhalation of the resuspended particles.

The worst case for the nonvitrified material with or without a barrier is excavation into the waste zone, shown in Table 1.14. While the barriers are designed to prevent surface erosion and plant or animal intrusion into the site, there is no way to predict whether future human populations may intrude into the waste zone. Although ISV cannot prevent an intrusion, it can mitigate its consequences.

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- U.S. Department of Energy. 1981a. Environmental Protection, Safety, and Health Protection Programs for DOE Operations. Order 5480.1A, Chapter XI, Washington, D.C.
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TABLE 1.14. Public Dose Commitments for Far-Term Intrusion, rem

	Year 1,000		Year 10,000	
	1st Year ^(a)	50 Year ^(b)	1st Year ^(a)	50 Year ^(b)
Drilling				
Unmodified site	24	880	16	550
Vitrification and engineered barrier	6	15	3	8
Engineered barrier	24	880	16	550
Excavation				
Unmodified site	48	1600	33	1100
Vitrification and engineered barrier	0.006	0.02	0.003	0.008
Engineered barrier	48	1600	33	1100
Vitrified curio ^(c)	0.2	10	0.1	5

(a) Lung dose.

(b) Bone dose.

(c) Total body dose.

1.3 DEFENSE BYPRODUCTS UTILIZATION AND PRODUCTION PROGRAM (AR-05-15-25 - 80576/GE-03-47-03 - 80401)

The objective of this program is to identify applications for nuclear byproducts and to develop techniques for recovery of these materials. Emphasis in FY 1983 is focused on recovery and potential applications of fission-product strategic noble metals, development of advanced isotope-fueled power production devices, and demonstration and deployment of radioisotope-powered lights in the far North.

Summary

The development continued on a melt casting process to produce high-density strontium fluoride for heat and power sources. The processing steps and parameters were defined. Techniques for condensing the volatile components were investigated that result in a significantly cleaner vacuum chamber. Densities of 4.1 g/cm^3 or better are reproducibly achieved, and purification by reducing the chromium, iron, and zirconium was confirmed. Removal of the volatile impurities was less successful in later tests than previously observed; experiments are continuing to resolve this apparent inconsistency.

Development of high-efficiency isotope power sources continued, with specific designs of Stirling generators proposed. Several designs of ^{90}Sr heat sources have been developed and modeled. A 1000- W_e power generator would require about four 850 W_t ^{90}Sr capsules, powering a Stirling generator with 30% efficiency. A thermal analysis indicates that adequate heat is transferred via a copper heat-transfer block of about 30 cm dia. With this design, heat at 640°C can be transferred to the generator without exceeding a strontium fluoride-inner capsule interface temperature of 800°C . A 1000- W_e

radioisotope-powered thermomechanical generator with a lead gamma shield would weigh less than 3000 kg.

Tritium-powered lights developed by Oak Ridge National Laboratory have been tested at military airfields in the contiguous U.S. and in Alaska. Planning has been completed for testing advanced tritium-powered light fixtures at both military and civilian airfields in Alaska this winter. These lights have the potential of providing relatively inexpensive lighting for remote airfields that have previously been unlighted.

Four techniques have been investigated for recovery of strategic noble metals from nuclear fuel reprocessing waste. These include 1) lead extraction during vitrification of HLW, 2) adsorption on chelating agents attached to activated carbon, 3) precipitation during sugar denitration, and 4) reduction using amine-borane reducing resins. Screening tests using an amine-borane reducing resin indicate that palladium was readily recovered but rhodium and ruthenium were not. A single experiment with precipitation during sugar denitration indicated that palladium could also be recovered by this technique.

Strontium-90 Fuel-Capsule Development

This program is to develop a densification process and the necessary equipment by which the ^{90}Sr fluoride prepared in the Hanford Waste Encapsulation and Storage Facility (WESF) can be densified and encapsulated to significantly higher power density than is currently feasible at WESF. The highest-wattage capsules currently held in the WESF storage basins have strontium fluoride densities of 3.2 to 3.7 g/cm^3 (75 to 85% TD) and thermal power outputs of from 660 to 760 W.

In the previous report in this series, preliminary results from both melt-casting and hot-pressing densification methods were reported. An analysis comparing the two methods for this application was done, and the results are given in Table 1.15. Hot pressing is superior to melt casting in three areas: it is a developed technology, it has been used in hot cells for many years, and it requires a significantly lower temperature and less off-gas cleaning.

Although melt casting is done at a somewhat higher temperature, operating at atmospheric pressure or less leads to a significantly simpler process. No high-pressure equipment or hydraulic fluids are required;

thus the in-cell operation and maintenance may be simplified. The greatest advantage of melt casting over hot pressing is the potential for purification during the melt-casting process. The preliminary decontamination factors observed appear sufficient to remove most initial impurity. Furthermore, melt casting appears capable of removing from 80 to 95% of the decay-product zirconium present in stored strontium fluoride. Such purification may result in an increased power density of up to 15% in melt casting of SrF_2 from capsules currently in the WESF storage basin. This purification is in contrast to a probable small increase in impurity content that occurs during material handling prior to hot

TABLE 1.15. Comparison of Melt Casting and Hot Pressing for Use in WESF

Areas of Comparison	Melting Casting	Hot Pressing
Probability of successful development for use in WESF	High	High
Product density	>95% TD	>95% TD
Equipment off-gas control	Requires careful off-gas cleaning	Less off-gas cleaning requirement than melt casting
Chemical purification	Has potential for significant purification	Has potential for slight increase in impurity contamination
Product ingot dimensional control	Adequate	Very good
Effect on WESF throughput	High probability of adequate throughput	Would reduce throughput
Equipment operability in a hot cell	Comparable to current WESF operations	More complicated than melt casting
Equipment maintainability in a hot cell	Comparable to current WESF operation	More complicated than melt casting
Effect on preparation of feed powder	Can probably eliminate current 1100°C drying step	Requires dry, uniform powder
Capsule compatibility	Potential for improved capsule compatibility due to reduced impurities	
Capsule power density	Significantly increased power density because of purification	

pressing. Melt casting is believed to have a higher throughput and can digest a lower quality feed material than can hot pressing. For these reasons, melt casting was selected for further development.

The melt-casting processing steps, as they would be conducted in WESF, are shown in Figure 1.6. As noted, provision is made for processing strontium fluoride from current operations or from reprocessing encapsulated material now in storage. The WESF cells in which the separate processing steps would be performed are shown. Those steps which have the highest potential for releasing strontium fluoride dust are confined to C Cell. The welding, nondestructive examination (NDE), and decontamination steps would be conducted

in the same cells and with the same equipment currently used for those functions.

The melt-casting operations would involve the following steps:

1. A melting crucible, loaded with SrF_2 powder, is placed in the open vacuum chamber above an empty casting mold, and the vacuum chamber is closed.
2. The vacuum chamber is evacuated and back-filled with argon to a pressure <1 atm, and the vacuum valve is closed.
3. The crucible and mold are induction-heated to 1350 -to- 1500°C to melt the powder.
4. The molten strontium fluoride is held at a fixed temperature and argon pressure for a preselected time, after which the freeze

FIGURE 1.6. Melt Casting of SrF_2 in WESF - Unit Operations

valve at the bottom of the crucible is opened, and the molten salt is drained into the ingot mold.

5. The temperature of the casting mold is reduced in such a way that the strontium fluoride solidifies from the bottom to the top.
6. After complete solidification is achieved, the vacuum chamber is cooled to ambient temperature, the pressure adjusted to 1 atm, the furnace opened, and the crucible and mold are removed.
7. The cast ingot is removed from the mold, cropped in length, and sized if necessary.
8. The crucible, mold, and furnace are cleaned and prepared for the next run.

The strontium fluoride charge cannot be melted in a vacuum because volatile impurities eject too much powder from the melting crucible. Aluminum, sodium and potassium fluoride impurities appear to vaporize from the charge and condense on the cold inner surface of the vacuum chamber. Iron and other reducible metal impurities are reduced to metal, which adheres to the inside surface of the carbon melting crucible. Zirconium may be removed by the same mechanism. The operating parameters being investigated to optimize the process and product are as follows:

- Operation of the freeze valve.
- A vacuum outgassing in step 2 at 500 to 1000°C.
- Optimum time, temperature, and pressure for holding the charge in molten condition prior to casting in step 4.
- Optimum temperature of the charge and the mold for casting.
- Optimum method for producing directional solidification in step 5.

- Optimum geometry of the casting mold to yield right circular cylindrical ingot with dimensions within acceptable tolerances.
- Use of a cold cap above the crucible to condense and collect volatile impurities and any strontium ejected from the charge.

In the initial design of the graphite melting crucible drain system, an extension was machined on the bottom of the crucible with the drain channel through the extension. A water-cooled copper finger was fabricated to fit against the opening in the bottom of the extension and cool the extension sufficiently to freeze a strontium fluoride plug in the drain channel during the melting and outgassing steps. The system always worked properly in the freeze cycle, but melting of the plug and draining of the crucible by withdrawing the cold finger was a little unpredictable. Rather than put a separate induction coil around the extension, the crucible was modified by removing the extension and machining a rounded groove into the flat, external bottom face of the crucible from the center hole to the edge as a track for the cold finger. In ten tests, the crucible drained within 30 seconds after the cold finger was withdrawn from the drain hole.

Melt-cast strontium fluoride cylindrical ingots with densities of 4.1 g/cm³ or higher have been obtained with good repeatability using the bottom-casting method. The chemical purification obtained in three castings is summarized in Table 1.16. The poor DF from volatile impurities in the third ingot is believed to be due to a shorter time at molten temperature in the melting crucible.

TABLE 1.16. Impurity Removal During Melt Casting of Nonradioactive Strontium Fluoride

Impurity Element	Process Decontamination Factor (DF)		
	Ingot 1	Ingot 2	Ingot 3
Al	3	3	1
Ba	1.5	1.5	1
Ca	1	1	1
Cd	60	60	1
Cr	6	9	2
Cu	3	1.5	-
Fe	10	13	9
K	1.5	1.5	-
Mg	1	1	1
Mn	1	1	1
Mo	3	3	-
Na	180	180	1
Ni	3	7	1
Si	1	1	-
Ti	7	7	-
Zn	2	2	-
Zr	5	8	8

$$\text{Decontamination Factor (DF)} = \frac{\text{Impurity Concentration in Feed Powder}}{\text{Impurity Concentration in Cast Ingot}}$$

Radioisotope-Powered Thermomechanical Generator (RTMG) Development

The conversion efficiency of radioisotope-powered thermoelectric generators is limited to about 9%. On the other hand, modern thermomechanical generators such as a free-piston Stirling engine directly coupled to a linear electrical generator have demonstrated conversion efficiencies of 33% with a 1 kW_e output. The purpose of this program is to procure a 1000 to 1500 W_e free-piston Stirling generator that is designed and built for long-life performance and interface it with a highly efficient heat source containing four 850 to 900 W_t redensified strontium fluoride

capsules. A second purpose is to test the RTMG under field conditions to demonstrate maintenance-free operation for 5 years or more. Successful completion of this program is intended to demonstrate that isotope-powered, dynamic generators can produce electricity reliably and still take advantage of a much higher efficiency.

The program will provide a technology that will increase by three- to tenfold the amount of useful electrical power that can be generated from existing inventories of the radioisotopes. The data base and experience gained in this program can be extended to follow-on RTMGs that are designed and constructed to meet the requirements of specific missions. RTMGs in the 5 kW_e range are feasible extensions of current technology as are thermomechanical generators (TMGs) in the 25 to 50 kW_e range powered by small, special-purpose nuclear reactors.

The feasibility of procuring a thermomechanical generator with the required performance characteristics was evaluated by issuing a request for proposal (RFP) to ten high-technology companies. The RFP technical requirements are summarized in Table 1.17. Bids that meet or exceed the technical requirements were received from two companies, and positive expressions of interest were received from two additional companies. A final decision on the RFP is delayed pending DOE FY 1984 and FY 1985 funding decisions.

A conceptual design of nominal 1000 W_e RTMG has been prepared and modeled by a computer code. Preliminary temperature and thermal-flow calculations have been made on the base design and on several variations to demonstrate feasibility of the concept. The design is shown in Figure 1.7 and the computer analyses are summarized in Table 1.18. For conservatism, the measured performance of

TABLE 1.17. Summary of Performance Requirements in Request for Proposal

TMG Required Performance	And/or Basis	
	Item 1	Item 2
Delivery date	3 mo	18 mo
Power output	100 to 150 W_e	1000 to 1500 W_e
Thermal to electrical conversion efficiency	>15%	>30%
Maintenance-free operating life	5 yr	5 yr

an existing Stirling generator (23.5% at an input temperature of 700°C) was used for the calculations rather than the higher efficiency of an advanced generator specified in the RFP. The capsule outside surface temperature was limited to 750°C to ensure that the inner capsule surface temperature would not exceed 800°C. The results show that satisfactory heat flow and temperature can be achieved using this concept. An RTMG of this design would produce about 1100 W_e when the low-performance generator used in the calculations is replaced by a modern, high-performance generator (greater than 30% conversion efficiency) such as those proposed in response to the RFP.

A thermal analysis was performed to evaluate temperature changes that would occur if the generator stopped and no alternate heat dumping system were provided. In this design, melting of the thermal fuse floods the vacuum foil insulation with helium and destroys its thermal insulation properties. Figure 1.8 shows the temperature changes that would occur in this event, assuming use of a fuse that melts at 850°C. The maximum and steady-state temperatures of the lead shield are 225°C and 173°C, more than 100°C below the melting point of the lead.

FIGURE 1.7. Strontium-90 Powered Thermo-mechanical Generator

Radioluminescent Lights Development

Radioluminescent lights have been under development for a variety of purposes. Early models of these used promethium and tritium to excite a phosphor to produce instrument, identification, and emergency lighting. Recent developments using tritium, advanced phosphor, and other technology have produced lights suitable for marking and lighting aircraft runways, highway marking, and marine navigation, as well as for other purposes. This work is sponsored by the Department of Energy, Department of Defense, and the State of Alaska. Oak Ridge National Laboratory (ORNL) and Pacific Northwest Laboratory (PNL) are the participating DOE National Laboratories.

Several meetings of the Technical Working Group have been held to evaluate advanced

TABLE 1.18. Summary of Preliminary Thermal Analyses

Computer run number	1	2	3	4	5	6	7
Min. temp. of generator interface, °C	634	634	638	634	639	643	634
Bottom of heat transfer block, °C	736	746	751	741	717	646	748
Generator gamma shield material	Cu	Cu	Cu	Cu	Cu	Cu	W
Copper heat transfer block dia, cm	31	30	30	30.5	34.1	22.4	31
Number of vacuum foils	6	6	12	6	6	6	6
Vac. foil heat loss, W	59	58	29	58	62	32	56
Heat dam thickness, cm	0.06	0.06	0.03	0.06	(1)	(1,2)	0.06
Heat dam heat loss, W	79	76	38	77	0	0	79
Heat source efficiency, %	96	96	98	96	98	99	96
Electrical power output, W	775	775	790	775	794	805	776
Overall efficiency, %	22.8	22.8	23.2	22.8	23.4	23.7	22.8
Fuel assembly wt, lb	6385	6179	6179	6282	7043	4724	5845

- Notes: 1 - Generator cylinder is part of the vacuum insulation envelope. That part of the inside surface of the vacuum insulation that extends past the fiber insulation in Figure 1.7 has a very high temperature differential and is called a heat dam. In this variation, structural changes are made that eliminate such a thermal leakage path.
- 2 - Heat pipes are imbedded in the copper heat transfer block. The effective thermal conductivity of the transfer block is increased a hundredfold.

FIGURE 1.8. Temperature Changes if Generator Stops

tritium-tube designs, parabolic and other reflectors as a means of enhancing the visual acquisition and identification for runway-threshold and edge-lighting use. In addition, planning for long-term testing of runway lighting and marking at both military and civilian airfields in Alaska this winter has been completed at these meetings. As a result, tube and fixture designs have been developed at ORNL which when appropriately configured for runway-threshold lighting can be acquired from 5 to 6 miles. These configurations can be seen in sufficient detail to identify each side of the runway threshold at 4 miles. Thus, the USAF military airlift command requirement that the lights be acquired and be visible from 4 to 6 miles can be met, and deployment of a complete runway configuration for a pre-Alaska evaluation is being conducted in early November. G. A. Jensen is a member of the Technical Working Group and will continue to participate in this effort.

Noble Metal Recovery and Use

Isotopes of the noble metals ruthenium, rhodium and palladium are byproducts of nuclear fuel burnup in reactors which produce plutonium at defense facilities or generate electricity at commercial power plants. Noble metals have strategic value sufficient to warrant their recovery from spent nuclear fuel reprocessing wastes. A lead-extraction process coupled to the high level liquid waste (HLLW) vitrification process has been developed to a considerable extent and demonstrated for noble metal recovery from HLLW. Use of this process rests upon whether waste vitrification will be used in Hanford PUREX facilities and upon results of further developmental studies. Additional exploratory

work is needed to establish 1) where noble metals concentrate in PUREX and in what quantities, 2) their chemical properties, and 3) alternative methods for recovery. The present emphasis is on the identification and evaluation of alternative processes and other related studies.

Purex flowsheets (Allen, Jacobs, and Reberger 1983) were examined to select the liquid waste streams that appear to offer the best opportunity for recovery of fission product noble metals. The candidates selected were LWW (concentrated first-cycle waste), ZAW (zirflex acid waste) formed by sugar denitration of LWW, and ZAW following neutralization. The choice of a waste stream would depend on the specific recovery process that would be used.

Three potential processes have been identified to date through patent and other literature evaluations. The first process is based upon a patent (Moore 1974) granted to PNL. In this process, liquid acid waste is contacted in sequence with column beds of activated carbon that have adsorbed different chelating agents specific for the metal to be recovered. The second process is based upon a patent (Campbell and Buxton 1981) granted to ORNL. In this process, palladium precipitates during mixing of a denitrating sugar solution with the waste solution heated to reflux temperature. The third process uses a highly porous, amine-borane, reductive resin placed in columns to selectively remove noble metals from pregnant liquids.

Base formulations for two simulated acid-waste solutions were devised, the first to simulate LWW of PUREX, the second, a typical commercial HLLW. The base formulations are given in Table 1.19. The key chemical compounds used for the formulation were primarily nitrates. Preparation of the simulated

TABLE 1.19. Base Formulations for Simulated Acid-Waste Solutions

PUREX 1WW		Commercial	
Element or Ion	Concentration, g/L	Element or Ion	Concentration, g/L
H ⁺	1.12	Rb	0.85
F ⁻	3.43	Sr	2.36
Al ⁺³	22.5	Zr	9.67
NO ₃ ⁻	215	Mo	11.22
Na ⁺	2.24	Ru	5.96
SO ₄ ⁻²	16.0	Rh	1.03
Cr	0.80	Pd	3.40
Ni	0.47	Fe	2.79
PO ₄ ⁻²	0.022	Ag	0.22
Zr	0.29	Cd	0.22
Cd	0.0011	Ce	7.18
Mn	0.092	Ba	3.71
Rb	0.022	PO ₄ ⁻²	2.4
Sr	0.061	Ce	14
Ru	0.089	Nd	14
Rh	0.024	Cr	0.62
Pd	0.017	Ni	0.29
Ag	0.0009	Te	1.54
Sn	0.0013		
Te	0.018		
Cs	0.13		
Ba	0.068		
Ce	0.25		
Nd	0.25		
Fe ⁺³	5.67		
Mo	0.16		

solutions was difficult; i.e., some compounds used dissolve only partly, or precipitation would occur following dissolution when the simulated waste solution cooled to room temperature. A similar precipitation of solids may occur with real solutions in actual spent fuel reprocessing operations.

In screening experiments using the amine-borane resin, small amounts of the resin were mixed in flasks with 100 mL of simulated PUREX 1WW solution; the materials were shaken

for 1 hr at about 25°C, separated, and then the liquid and used resin analyzed by induction-coupled plasma spectrophotometry (ICP). Approximate noble metal recoveries from simulated 1WW are shown in Table 1.20.

Recovery of palladium from solution was satisfactory; recovery, however, of rhodium and ruthenium was not. The percents recovered (shown in Table 1.20) are based on analyses of the metal sorbed on the resin and agree with those calculated by difference from analyses of the supernatants. However, about 24 wt% of the ruthenium originally in the test solution appeared to be removed but was not found in the resin. Ruthenium may have been lost to resin rinses which have not been analyzed; it is unlikely that it was lost by volatilization of the tetroxide as the test temperature was 25°C. Amine-borane resin was reported to reduce palladium and rhodium, but not ruthenium, in the manufacturer's qualitative screening tests (Manziek 1982). More work is needed to learn why the rhodium was not reactive.

Further testing with the amine-borane reducing resin focused on determining whether equilibrium had been reached and whether longer contact times would result in more complete palladium recovery. These tests revealed that increasing the contact time from 1 to 24 hr substantially reduced the recovery rather than increasing it; this

TABLE 1.20. Noble Metal Recoveries from 100 mL of Simulated PUREX 1WW at 25°C Using Amine-Borane Reducing Resin

	Resin Weight Used With 100 mL of Test Solution, g		
	0.25	0.50	1.50
	Recovery, wt%		
Palladium	38	48	57
Rhodium	0	0	0
Ruthenium	0	0	0

1.0 WASTE STABILIZATION

The objective of the Waste Stabilization activities is to develop technology to recover or immobilize and package radioactive wastes from nuclear fuel cycle facilities for useful applications or for ultimate disposal.

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2.0 NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER

The objective of the Nuclear Waste Materials Characterization Center (MCC) is to provide an authoritative data base that will include information on the components of the waste emplacement package (the spent fuel or processed waste form and the engineered barriers), their interaction with each other, and the effects of their environment. The MCC works with waste-form producers and repository developers to standardize test methods and obtain materials data and submits these to the Materials Review Board (MRB). After test methods and data have been approved by the MRB, the MCC publishes the approved methods and data in the Nuclear Waste Materials Handbook.

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2.0 NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER

(AR-05-15-10/DB-60-20-20 - 80145)

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SUMMARY

Two test methods, MCC-12P Test Method for Determining Density Changes in Actinide-Doped Waste Forms and MCC-103P Stress-Corrosion Cracking Susceptibility Test Method, were added to the Nuclear Waste Materials Handbook. The first MCC data package, MCC-D1S One-Year Leach Test Data for PNL 76-68, was added to PNL-3990. In a meeting in Chicago on July 25-27, 1983, the MRB Procedures Panel acted on MCC-3 and MCC-4, and the MRB as a whole acted on MCC-1 (Rev. 1), MCC-D1 and MCC Guidelines for Accuracy and Precision of Test Data. The MCC was instructed to make minor modifications in MCC-4 and MCC-D1 before resubmittal to the MRB Procedures Panel and MRB as a whole, respectively. The other submissions were approved, providing the MCC make certain agreed-upon minor modifications.

Two repository relevant test methods, MCC-14.1 Materials Interactions Test Method (Basalt Static System) and MCC-105.1 Test Method for Long-Term Corrosion in Repository Environment (Basalt Static System) were submitted to the OTC-MRB.

Manufacture of 500 lb of reference nonradioactive glass was completed satisfactorily by Schott Optical Glass, Duryea, Pennsylvania. After testing, the National Bureau of Standards certified that the glass met or surpassed all purchase specifications for homogeneity, composition and residual

strain, and at the end of the reporting period was shipping the glass to PNL, where it will be developed by the MCC as a reference material for use with MCC-1, 2 and 3 leach tests.

Two radioactive glasses were prepared during this reporting period for use by the repository waste package projects as MCC-approved testing materials. One (designated ATM-5) is a fully loaded 76-68 waste glass prepared from calcined Nuclear Waste Vitri-fication Project (NWVP) waste solution. The second glass (designated ATM-6) was prepared to match a proposed Barnwell glass composition, with a selected actinide and fission-product content. Requests for supplies of ATM-5 and ATM-6 have been received from ONWI and BWIP, respectively. In addition, arrangements were completed for acquisition of ten H. B. Robinson spent fuel rods, to be transferred from EG&G to the MCC for characterization and distribution to the repository projects as a reference testing material.

ADMINISTRATION

Two additions were made to the Nuclear Waste Materials Handbook. At the beginning of the reporting period MCC-103P Stress-Corrosion-Cracking Susceptibility Test Method was mailed to custodians of the Handbook. At the end of the reporting period MCC-1P (Rev. 1) Static Leach Test Method and

MCC-D1 One-Year Leach Test Data for PNL 76-68 were mailed. The MCC-D1 data package is the first entry in the data volume of PNL-3990.

TASK 1 - WASTE MATERIALS INTERACTIONS

MCC-14 Materials Interactions Test Methods

Although knowledge of comparative chemical durabilities of waste forms and the waste form/water reactions is important, this knowledge does not enable prediction of the long-term behavior of a specific waste form in a repository environment. The understanding of the long-term behavior is a much more complex undertaking, which requires measurement of the effects of other waste package components under simulated repository conditions. Tests that include these effects have come to be called interactions tests and are being developed and conducted to various extents by the site projects and potential waste form producers.

In FY 1983, one effort of the MCC was to collect and codify interactions test methods that yield data needed for determining radionuclide release rate as part of the overall waste package performance assessment. Such assessments are a part of the proposed repository licensing requirements.

In June 1983, the MCC submitted an interactions test method (MCC-14.1, Basalt) to the OTC-MRB. This test method was based on procedures and techniques developed and in use by the Basalt Waste Isolation Project (BWIP). Before submission, the test was reviewed by PNL and BWIP staff, with necessary changes incorporated in the final version. In July, R. G. Strickert made a presentation to the Materials Review Board

on the purposes and experimental techniques of MCC-14 interactions test methods.

Interactions test methods from other site projects are in various stages of development. Because of inherent differences in the geologic sites, each will probably use a different waste package design, and each will have some unique testing requirements. However, MCC-14.1, and the other tests in general, will use agitated batch or autoclave methods. When anoxic conditions are needed, the tests are run under an argon atmosphere. Because analysis at elevated temperatures is not currently possible, sampling of the solutions at their experimental temperature will be employed. This is done primarily to reduce the effects of quenching on solution concentrations. Approved Test Materials (ATM) used in the tests will be supplied by the MCC.

As shown in Figure 2.1, the goal of interactions testing is to produce data that, when used in conjunction with mathematical models, will yield predictions of long-term waste package behavior in a repository. The MCC-14 test methods are designed primarily to evaluate radionuclide concentrations in ground-water solutions contacting a given waste form in the presence of one or more waste package components (and the host rock), under conditions which simulate, as closely as possible, repository conditions (e.g., temperature, radiation). The tests also will provide data on the other elemental concentrations in solutions which have contacted the waste package materials over a period of time. Analytical data are also to be obtained on solid phases before and after interactions testing. Test temperatures can range up to 300°C and pressures up to 30 MPa (300 bars).

FIGURE 2.1. Interactions Testing - Input and Output

Because of the large number of experimental parameters that may be varied or held constant, a full factorial test matrix would be infeasibly large. Rather, a statistical approach toward establishing testing priorities is to be used, based on designs such as fractional factorials. Although the MCC-14 test methods will have to allow user discretion in selecting some initial test conditions, each method (e.g., MCC-14.1) will also include a benchmark test in which all relevant parameters are specified for a site-related reference condition. The benchmark test will be used to validate the test method and to quantify the uncertainty

in the test data. Benchmark tests will be conducted by the MCC and the respective site project.

High-Temperature Solubility Methods

In previous MCC-1 leach testing, certain elements (such as plutonium) were found to reach steady-state concentrations in less than 3 months, while alterations in the glass surface layer continued. Rai and Strickert (1980) suggested that specific Np and Pu solid phases may control these actinide concentrations in aqueous suspensions of doped borosilicate glass. Because the

thermodynamic data base for important actinide elements is incomplete, the NRC (1983) and the National Academy of Science (1983) have recommended that temperature-dependent solid phase solubilities and complex stability constants for selected, important radionuclides be determined up to at least 175°C for the anticipated ionic strengths. Such data would be important in predicting the maximum long-term release rate of actinides from a waste package.

Efforts were initiated in Task 1 during FY 1983 to design and refine experimental procedures for measuring the equilibrium aqueous solubilities of radionuclides containing solid phases at elevated temperatures. The uranium system was selected for this work because:

1. Uranium is present in nuclear reactor wastes.
2. The solutions are not highly radioactive and thus are easier to work with during developmental stages.
3. The solubility data for uranium solids will be valuable for assessing maximum concentrations of uranium in ground water and surface water.

The studies to date have involved measuring the solubility of the U(VI) hydroxide solid $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ (schoepite). The uranium (VI) hydroxide occurs in natural environments and has been identified in laboratory and leaching studies (Wang 1981) of UO_2 (a major matrix component of spent fuel).

Schoepite was synthesized by aging amorphous UO_3 in distilled water. X-ray diffraction analysis was used to confirm the identity of the material at the start and conclusion of each experiment. The reaction vessel previously described (Chikalla and Powell 1983) was modified to avoid caking of schoepite on the pH electrode and to allow

more reliable pH measurements of solution aliquots. Some solubility experiments were conducted inside an argon atmosphere (CO_2 -free) chamber. Uranium concentrations of filtered aliquots were measured by a laser-induced fluorescence technique. Several experiments at different pH values were conducted.

The measured total filtered uranium concentrations at 25°C are plotted in Figure 2.2 as a function of reaction time. Based on these values, one would at first assume that steady-state conditions (i.e., equilibrium) were not achieved between schoepite and water during the experimental time. However, the solubility of schoepite is strongly dependent on pH, which did vary in these poorly buffered systems. Therefore, the evaluation of equilibrium is best accomplished by calculating the activities of the uncomplexed and complexed aqueous uranium species. Ion activity products are then formulated from these activities and the stoichiometry of the solid phase whose solubility is assumed to control the concentration of the dissolved constituent of interest.

The geochemical code MINTEQ (Felmy et al. 1983a,b) was used to calculate the activity product (AP) values for the schoepite reaction

by substituting the activities of the species UO_2^{2+} and H^+ (pH) calculated from the analytical data into equation (2). The calculated log AP values

$$\text{Log AP} = \text{Log} (\text{UO}_2^{2+}) + 2\text{pH} \quad (2)$$

are plotted in Figure 2.3. Except for a few errant points, the calculated values cluster

FIGURE 2.2. Measured Concentrations (mg/L) of Total Dissolved Uranium (0.015 μ m Filtrate) as a Function of Dissolution Time for Schoepite Experiments at 25°C. (Filled squares represent data from Experiment 1; filled circles, from Experiment 2; and filled triangles, from Experiment 3.)

at approximately $\log AP = 5.5 \pm 0.2$ and are in good agreement with the thermodynamic data of Langmuir (1978) for schoepite. From these results the solutions taken from these dissolution experiments appear to be in equilibrium (even after a couple of days) with schoepite--a conclusion not obvious from the total analytical concentrations of dissolved uranium.

The experimental methods developed are now being employed at 90°C, at alkaline pH values, and from oversaturation conditions.

Interfacing with Modeling Activities

The MINTEQ geochemical code was used during the reporting period to calculate the aqueous speciation and ion activities for the schoepite solubility solution analyses (discussed above) and for data from various MCC leach tests.

Results from some of these calculations on data from 1-year MCC-1 leach tests at 90°C are discussed in a recent report by Strachan, Krupka and Grambow (1983).

FIGURE 2.3. Calculated Activity Products (AP) for Schoepite from Dissolution Experiments at 25°C. (Filled squares represent data from Experiment 1; filled circles, from Experiment 2; and filled triangles, from Experiment 3.)

TASK 2 - DS CORROSION

Test Method Development

MCC-101 Static-Immersion Corrosion Test Method

This test method has been revised according to recommendations by the OTC-MRB and will be published in PNL-3990. The method has been the precursor to site-specific

MCC-105 tests, for which it was revised to be applicable to repository environments.

MCC-102 Unstressed, Flowing, Immersion Corrosion Test Method

This test method was revised according to comments by OTC-MRB and is ready for publication in PNL-3990. It will provide the basis for further development of MCC-105.4 (Flowby Test System) for application to a basalt repository.

MCC-103P Stress-Corrosion-Cracking Susceptibility Test Method

No further development of this test method has occurred since approval by MRB and publication in the Handbook at the beginning of this reporting period.

MCC-104S Stress-Corrosion-Cracking-Rate Tension Test Method

This method was reviewed by three MRB members and is being developed further. The MCC is obtaining data to substantiate this method and has obtained comments through the ASTM E24 committee on the method. Testing and development of experimental techniques to support MCC-104 are continuing. A workshop with site investigators and experts in the testing of stress-corrosion cracking is being planned for early FY 1984.

MCC-105 Test Method for Long-Term Corrosion in Repository Environments

Test methods are being codified for basalt, salt, and tuff repositories. Because the tests for these three sites are different, the MCC will submit site-specific methods separately to MRB. Five test methods have been identified so far, designated MCC-105.1 through MCC-105.5.

The MCC has the position that once initial agreement is reached between MCC and site investigators, the MCC will initiate benchmark testing necessary to substantiate data quality and reliability.

MCC-105.1 Basalt Static System. A method was codified shortly after the workshop in February and was submitted to BWIP for review. The test consists of benchmark conditions: temperature = 100 and 200°C,

radiation level = 0 and 10^4 R/hr; times = 120 and 300 days; media = synthetic ground water and basalt; testing will be done in small metal reaction vessels. The initial review was completed by BWIP, and MCC revised the method according to comments and submitted it to MRB. The ATM will be A27 cast steel.

MCC-105.2 Tuff Static System. The development of a method(s) for tuff is in a preliminary stage, and NNWSI investigators have requested the method be submitted to MRB only after data have been obtained. The MCC prepared a draft of MCC-105.2 for review by NNWSI and has not received formal response to date. The MCC will continue to review NNWSI progress in definition of corrosion testing in order to modify the preliminary drafts of MCC 105.2.

MCC-105.3 Salt Static System. A draft of MCC-105.3 was reviewed informally by ONWI investigators prior to a request for formal review by ONWI. Many changes in the method were incorporated and the method was transmitted to ONWI for agreement before MCC initiates benchmark testing. The test consists of benchmark conditions: Temperature = 100 and 150°C; times = 120 and 300 days; Radiation level = 0 and 10^3 R/hr and media = dried, crushed "brine A" with limited water addition. The proposed test vessel is a Zr-2.5 Nb alloy pressure vessel of 300 mL capacity. The ATM will be ASTM 216-77 Grade WCA cast steel.

MCC-105.4 Basalt Flowby System. Investigators for BWIP have requested MCC to codify a test method wherein the corrosion specimens are placed in packing material (basalt + bentonite) such that water access is diffusion-limited to simulate long-term

post-closure conditions in a basalt repository. The MCC will consult BWIP subcontractors and BWIP investigators for agreement on the method before codification and submittal to MRB.

MCC-105.5 Basalt Water Vapor System. Investigators for BWIP have requested MCC to codify a test method wherein the corrosion specimens are placed in a slowly refreshed water vapor environment to simulate conditions in the operational period of the basalt repository. The MCC will begin codifying this method in FY 1984.

Benchmark Testing

The MCC plans to initiate benchmark testing according to MCC-105.1 and MCC-104.3 in FY 1984. Testing according to MCC-105.2 will be initiated if the method becomes sufficiently defined. The MCC has procured pressure vessels for basalt and salt testing and has begun to set up equipment to initiate corrosion tests. A plan for data management and QA is being implemented.

TASK 3 - WASTE FORM CHARACTERIZATION

Test Method Development

Three test methods developed in Task 3 were reviewed at the MRB meeting in Chicago July 25-26. MCC-3 and 4 were reviewed by the Procedures Panel; MCC-1 (Rev. 1) was reviewed by the full board. MCC-1 (Rev. 1) and MCC-3 were approved; MCC-4 was returned to the MCC for further revisions. Details follow.

MCC-1P (Rev. 1) Static Leach Test Method

Revision 1 of this test method, which includes modifications that permit the use of highly radioactive waste-form specimens, was approved by the MRB with the understanding that the MCC would incorporate certain agreed-upon minor changes. The MCC also made some additional changes it believed were necessary to clarify the stepwise procedure to be used with actinide-containing specimens. At the end of the reporting period MCC-1P (Rev. 1) had been mailed to the MRB members for a phone ballot on the additional changes the MCC made to MCC-1P (Rev. 1).

MCC-3 Agitated Powder Test Method

This test method was approved by the MRB Procedures Panel with the understanding that the MCC would incorporate some agreed-upon minor changes. Those agreed-upon changes resulted in considerable rewriting, particularly of the supplementary data portion of the MCC-3 submission. This rewriting has been completed and the revised MCC-3 is in the final editing stage.

MCC-4 Low-Flow-Rate Leach Test Method

When this test method was presented to the MRB Procedures Panel for review at the Chicago meeting, it was pointed out that the MCC had made an error in the graphical treatment of the leach rates obtained at low flow rates. The MCC has replotted the leach rates and is preparing the revised MCC-4 for resubmission to the MRB Procedures Panel.

Foreign Travel

Denis Strachan spent the period from May 16, 1983, to August 5, 1983, at the Hahn-Meitner Institute as an exchange scientist. A joint leach testing experiment was conducted to determine the effect of dissolved magnesium using 76-68 and C31-3, which are U.S. and West German waste glass formulations, respectively. The MCC-1 leach test method was used with 0.001 M MgCl_2 and deionized water as leachants. An apparently nonprotective layer of sepiolite $[\text{Mg}_2\text{Si}_3\text{O}_6(\text{OH})_4]$ formed on the glass surfaces leached in 0.001 M MgCl_2 . Two papers will result from this collaboration with Hahn-Meitner Institut: "Leach Testing of Waste Glass Under Near-Saturation Conditions," which has been accepted for presentation at the Materials Research Society Meeting in November in Boston, and "Solubility Interpretation of Leach Tests on Nuclear Waste Glass," which will be submitted for publication in the journal Nuclear and Chemical Waste Management.

TASK 4 - REFERENCE MATERIALS AND ANALYTICAL METHODS

MCC-D1 One-Year Leach Test Data for PNL 76-68 Glass

Data Package MCC-D1, first submitted to the Materials Review Board (MRB) on August 2, 1982, was further revised three times in response to successive MRB written review comments, MRB Data Panel review meeting discussions, and full MRB review meeting instructions. The current revision is ready for submission again to MRB. At the same time a condensed version of the voluminous full data package has been prepared for publication in the MCC Handbook. Pending ap-

proval of the MRB of these revised data packages, the Handbook version of MCC-D1 has been published in PNL-3990.

MCC Accuracy and Precision Guidelines

The MCC Accuracy and Precision Guidelines were approved by the MRB for Handbook publication, following two revisions, in response to written comments and subsequently to instructions from the full MRB review meeting. Publication of the Guidelines in the Handbook is scheduled for the first quarter FY 1984.

Shielded Analytical Facilities for Characterization of Radioactive Nuclear Waste Materials

The three MCC shielded instruments for analysis of radioactive materials are all fully operational, and have been applied to nuclear waste materials. The scanning electron microscope was used in a study of radioactive TMI glass prepared for the Zeolite Vitrification Demonstration Program (ZVDP) and specimens have been prepared for SEM examination of radioactive MCC reference waste glass ATM-6. The ICP spectrometer was applied to solutions resulting from in-cell leach testing of ZVDP glass, analysis of the bulk ZVDP glass, and to analysis of the calcination product from NWVP solution used for MCC radioactive reference glass ATM-5. X-ray diffractometer specimens have been prepared from radioactive MCC reference glass ATM-6. The performance of all instruments has met or exceeded specifications. Applications to several other programs, as well as intensive use on MCC materials, is planned for FY 1984.

Reference Materials

ARM-1

Manufacture of the Approved Reference Material-1 (ARM-1) was completed satisfactorily by Schott Optical Glass, Duryea, Pennsylvania, and delivered to the National Bureau of Standards (NBS) for evaluation. NBS tested the glass for quality and homogeneity by measurements of refractive index, residual strain, bubbles and striae, and composition. The glass meets or exceeds all specifications for physical properties and homogeneity. Composition as determined by both NBS and MCC analyses is satisfactory for an MCC reference material. Therefore, the glass has been accepted for that purpose and has been shipped from NBS to MCC for archive storage and distribution. Further characterization analyses and MCC leach tests are scheduled to obtain MCC-certified performance data.

Radioactive Reference Glasses

Two radioactive glasses were prepared during this reporting period for use as MCC-approved testing materials. One (designated ATM-5) is a fully loaded waste glass prepared from calcined NWVP waste solution. Analysis of the NWVP calcine using the shielded ICP spectrometer revealed that it contained too much iron to qualify for use in a Barnwell-process glass. Therefore the calcine was used to prepare about 3000 g of 76-68 type glass instead, as a radioactive reference material related to the large body of 76-68 simulated waste test data already in existence in the U.S. and foreign laboratories. Requests for supplies of ATM-5 have been received from ONWI and NRC programs.

The second radioactive reference glass (ATM-6) was prepared to match a proposed Barnwell process composition, with selected actinide and fission product components included as listed in Tables 2.1 and 2.2. All other glass and waste stream constituents were added as nonradioactive isotopes in order to reduce subsequent analytical problems. About 3000 g of this material was prepared, of which 2000 g is assigned to the BWIP. Specially ground and sized powder specimens were prepared from some of the glass for BWIP's use, under direct funding from BWIP.

Characterization of ATM-6 was started. Complete characterization of both radioactive glasses is scheduled for the first quarter of FY 1984.

Reference Spent Fuel

Arrangements were completed for acquiring ten H. B. Robinson spent fuel rods, to be transferred from EG&G to MCC for characterization and distribution as an approved testing material (ATM-101). This spent fuel has

TABLE 2.1. Composition of ATM-6 Reference Glass

<u>Component</u>	<u>Wt%</u>
SiO ₂	48.0
B ₂ O ₃	9.0
Na ₂ O ₃	3.5
Li ₂ O ₃	4.5
Al ₂ O ₃	5.0
Waste ^(a)	30.0
	100.0

(a) Waste composition based on values reported in BNFP Waste Characterization and Waste Treatment by K. J. Anderson et al., PNL-3136/FR-01. Revised November 1982.

TABLE 2.2. Glass A: Dopant Concentrations in ATM-6(a)

Elements	Specific Radioactive Isotope(s)	Concentration of Dopants in Glass, g isotope/g glass	
		Radioactive Isotope	Stable Isotope
<u>Actinides</u>			
Uranium	(Depleted or natural uranium; 2.0E-2 g uranium per g glass)		
Curium	Cm-244	5.6E-7	--
Thorium	Th-232	1.0E-7	--
Neptunium	Np-237	3.2E-3	--
Plutonium	Pu-238	2.6E-5	--
	Pu-239 and/or	1.6E-4	--
	Pu-240		
<u>Fission Products</u>			
Technetium	Tc-99	2.6E-3	--
Lead	--	--	2.3E-5
Cesium	Cs-137	1.1E-4	7.6E-3
Samarium	--	--	7.9E-3
Cerium	--	--	1.2E-2
Tin	--	--	5.0E-4
Selenium	Se-75	2.5E-9	8.0E-5

(a) All other elements listed in the BNFP waste composition added as nonradioactive isotopes.

been selected as representative of a large fraction of the spent fuel currently on hand in the United States. The transfer from EG&G was begun with retrieving specific selected rods, puncturing to collect fission gas for analysis, sectioning into halves, and recapping the cut ends. Shipment of the rods to PNL/MCC for archiving, characterization and distribution is scheduled for October 10. All three NWTs programs have requested assignment of ATM-101 rods to their test work.

The report Spent Fuel Approved Testing Materials for Radionuclide Release Studies (PNL-4686) was completed. A limited distribution of comment copies is being made to NWTs program representatives and DOE/MIO

prior to final publication. In addition to providing criteria for selection of reference spent fuels and a review of possible sources of the reference material, the report presents a description of MCC's characterization of the fuel rods for use as a reference material. Characterization will begin as soon as the fuel is received at PNL. A significant amount of information on H. B. Robinson spent fuel characteristics is already available in the literature. The fission gas release data being obtained by EG&G before shipment will constitute the first analytical data for these ten specific rods.

Testing and Service

The radioactive glass prepared at PNL for the ZVDP was evaluated by MCC-established methods, in an activity funded directly by the ZVDP. Leach testing by MCC-1 Static Leach Test was emphasized; microstructure and composition were also investigated. Leach testing was conducted in quartz vessels designed for use in a specially constructed well-type oven in the PNL hot cells. Analyses were conducted with the MCC shielded analytical facilities.

Test results demonstrated mass losses after 28 days of leaching that are significantly lower (factor >2) for the ZVDP radioactive glass than for nonradioactive 76-68 glass and slightly lower than for nonradioactive ZVDP glass. Microstructure of the radioactive material was consistent with that observed in the nonradioactive material, and no second-phase components were detected. Details of test methods and results are contained in the report submitted to the sponsor, Zeolite Vitrification Demonstration Program Characterization of Radioactive Vitrified Zeolite Materials (PNL-4856).

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3.0 WASTE ISOLATION

The objective of the Waste Isolation Program at PNL is to support the National Waste Terminal Storage Program's efforts to develop the technology and facilities required for the safe and environmentally acceptable disposal of nuclear waste.

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3.0 WASTE ISOLATION

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3.1 OFFICE OF NUCLEAR WASTE ISOLATION
(ONWI)3.1.1 Waste Package Program
(DB-30-30-01 - 80597)

The main objective of the Waste Package Program (WPP) is to help provide the necessary data base on waste package components and multicomponent interactions to qualify a waste package for geologic disposal. Supporting this are the following more specific program objectives: 1) help provide a basis for meeting waste package performance standards; 2) provide input to waste package designers; 3) optimize and select structural barrier materials; 4) develop predictive models for waste package degradation and radionuclide release.

Summary

Based on work conducted during the past quarter, the following conclusions can be made:

- Without irradiation, the general corrosion of cast and wrought low-alloy ferrous materials in Permian Basin brine is not particularly severe; a corrosion allowance for 1000-yr service of ~25 mm (~1 in.) appears adequate.
- The 1000-yr corrosion allowance for low-alloy ferrous materials required under the test conditions of 1×10^5 rad/hr and 150°C Permian Basin brine would be ~200 mm, assuming that linear corrosion

kinetics of these materials under conditions more closely simulating those expected in a salt waste repository are required.

- The observed embrittlement of 1025 wrought steel in Permian Basin brine No. 2 at 150°C in slow-strain-rate tests has been shown to be due to the combined effects of hot brine and strain rather than to hydrogen embrittlement.
- Within experimental error, the solubility values for americium in brine, diluted brine, and deionized water are the same.
- Ductile iron scavenges actinides and technetium from spent fuel/brine leach tests, resulting in an order-of-magnitude decrease in solution concentrations.
- The gas pressure generated by radiolysis of Permian Basin salt brine is nearly 100 atm at equilibrium.
- The presence of ductile iron accelerates growth of crystalline phases in the glass/iron/brine system at 150 and 250°C. This is consistent with observations at lower temperatures.
- Preliminary alteration product analysis from 76-68 glass/ductile iron/brine interactions tests shows the presence of talc and sepiolite at temperatures of 150 and 250°C. This information is providing

- an explanation of the observed changes in solution compositions at these temperatures.
- Preliminary alteration product analysis from 76-68 glass/ductile iron/brine interactions tests shows the presence of talc and sepiolite at temperatures of 150 and 250°C. This information is providing an explanation of the observed changes in solution compositions at these temperatures.
 - Glass leach rate enhancement due to radiolysis appears to be temperature-dependent, with radiolysis becoming unimportant at temperatures $>90^{\circ}\text{C}$ with and without the presence of ductile iron.
 - The mechanism by which ductile iron accelerates leaching of 76-68 glass is thought to involve iron-silicate colloid formation, thereby reducing the activity of silicon in solution, which in turn causes increased silicon release from the glass.
 - Leaching tests with spent fuel in salt brine at 25 and 75°C, up to 60 days duration, show an insignificant effect of temperature on element release with or without ductile iron present.
 - Ductile iron has a large effect on the distribution of released uranium as determined from UO_2 -iron-brine interaction tests. In the presence of iron, the total amount of uranium released was not measurably increased, but the iron sorbed most of the uranium from solution. This occurred whether or not oxidized zircaloy was present. The amount of uranium released from spent fuel under identical conditions was two orders of magnitude more than that from UO_2 (unirradiated). It could be that radiolysis is having a major effect.
 - Tests with actinide-doped 76-68 glass in salt brine show the formation of actinide-containing true colloids.
 - Redox potentials measured in alpha radiolysis experiments on salt brine show that highly oxidizing conditions are formed.
 - Dissolving Permian Basin rock salt and NaCl samples in deionized water before and after gamma irradiation has not yielded major changes in solution chemistry in tests run to date. The evolution of chlorine has not been detected in statistically significant amounts.
 - Uranium solution concentrations pass through maxima after about 10 days at 150°C in either salt brine or deionized water. The most likely explanation is early dissolution followed by nucleation and growth of one or more new uranium compounds.
 - Uranium concentrations at 150°C in both salt brine and deionized water are similar after a 1-month exposure of UO_2 to these solutions.
 - Results from the solution radiolysis product code RADIOL show that dose rate is the parameter having the most profound effect on radiolysis product concentrations; an increase in dose rate causes a proportional increase in concentration of H_2 , e^- , H_2O_2 , $\text{OH}^\bullet$, HO_2 , and HO_2^- .
 - A review of literature regarding calculated single-ion-activity coefficients has shown that several calculational methods agree well enough to provide useful estimates. These will assist in the interpretation of test data and prediction of repository conditions.

Program Management

Program administration has focused on the following areas:

- The Waste Package Program Mid-Year Review was held at PNL. A complete review of the program, along with several laboratory tours, was given by WPP staff.
- WPP staff participated in three accelerated testing workshops on iron corrosion, chaired by R. W. Cote, at PNL.
- Discussions were held with R. W. Cote concerning the present program status and programmatic efforts for FY 1984.

Liaison activities have included the following:

- A WPP/MCC (Materials Characterization Center) meeting was held to discuss the current status of the MCC-14 draft procedures relative to testing in a salt environment.
- A formal request was sent to J. E. Mendel, manager of the MCC, requesting that HBR-II spent fuel be shipped by May 1983 to PNL for WPP testing in a salt environment.
- A meeting was held with BWIP (Basalt Waste Isolation Project) waste package and MCC staff, to discuss the use of spent fuel in waste package testing.
- A formal request was sent to J. E. Mendel, manager of the MCC, for preparation of a series of actinide-doped MCC-76-68 waste glasses for WPP use.
- WPP staff participated in a two-day meeting at PNL on waste package performance modeling with J. F. Kircher, G. Jansen, and G. E. Raines of ONWI.
- Discussions were held with Professor T. H. Pigford on waste package activities.

- A meeting was held with the MCC and NWTs (National Waste Terminal Storage) site representatives to discuss shipment of spent fuel by the MCC to Hanford. The results of this meeting were forwarded to ONWI.
- D. J. Bradley and G. L. McVay participated as observers during an IAEA (International Atomic Energy Agency) Coordinated Program workshop at PNL on waste form evaluation.
- Dr. H. Engelmann, Mr. Wuertz, and Mr. Jacobi, from the Federal Republic of Germany, visited PNL and discussed waste isolation activities with WPP staff.
- An MCC draft plan on "Spent Fuel Characterization Requirements for Use as MCC Approved Testing Materials" was reviewed. The results of this meeting were forwarded to ONWI.
- D. J. Bradley discussed the status of the Waste Package Program, test procedures, and interfaces with the MCC with J. Haugen and C. McPheeters of the Materials Integration Office.

Structural Barriers

General Corrosion Studies. The general corrosion data currently available on ferrous alloys in brines relevant to salt repositories derive from three primary sources: early PNL data, obtained from 250°C WIPP Brine A screening studies of various cast irons (Westerman 1980); Sandia National Laboratory studies emphasizing cast irons in 250 and 150°C Brine A (Molecke 1981, 1982); and unpublished PNL data obtained during the past year emphasizing the determination of the corrosion rates of ferrous materials in Permian Basin salt brine No. 1 and No. 2 at 150°C. The brine

compositions referred to are presented in Table 3.1. Permian Basin salt brine No. 1 and No. 2 are generally not considered to be as corrosive to ferrous materials as Brine A since the pH of Brine A decreases when the brine is heated, due to precipitation of magnesium compounds. The exact composition of the brine that will eventually contact the waste package in any given site is not known, as the composition of the brine in the inclusions migrating up the temperature gradient toward the hot waste package has not been analyzed.

A possibility exists that the inclusions may become enriched in magnesium during the migration; then, as a critical temperature range is reached, the magnesium may precipitate out, leaving a close equivalent of Brine A to interact with the waste package

overpack material. This scenario provides justification for Brine A environment studies. An accident scenario involving the ingress of aquifer water into a salt repository provides justification for studies of Permian Basin brine.

Studies of ferrous materials (cast irons and mild steels) in Brine A at 250°C, even in unirradiated, static autoclave systems, show high corrosion rates, ~40 to 70 mils penetration per year. These rates are plainly not tolerable in the current design concept utilizing a cast mild steel of several inches thickness.

On the other hand, recent PNL studies of ferrous materials in Permian Basin brine at 150°C show that they can be considered for overpack with the current waste package conceptual designs, i.e., a package with an

TABLE 3.1. Compositions of Simulated Salt Brines

<u>Ion</u>	<u>Permian Basin No. 1(a)</u>	<u>Permian Basin No. 2(b)</u>	<u>Brine A</u>
Na ⁺	123,000	123,000	42,000
Ca ²⁺	1,560	1,100	600
Mg ²⁺	134	122	35,000
K ⁺	39	39	30,000
Sr ²⁺	35	35	5
Zr ²⁺	7.8	7.9	--
Cl ⁻	191,000	191,000	190,000
SO ₄ ²⁻	3,200	1,910	3,500
HCO ₃ ⁻	30	23	700
Br ⁻	32	24	400
F ⁻	1.1	1.0	--
I ⁻	--	--	10
BO ₃ ⁻⁻⁻	--	--	1,200
pH	7.2(c)	7.05(c)	6.5

(a) The salt brine made up from a recipe derived from analyzing actual Permian Basin salt dissolved in distilled water to saturation.

(b) Permian Basin No. 2 is based on the composition of the supernatant fluid resulting from heating Permian Basin brine No. 1 to 150°C.

(c) Measured values.

unprotected low-carbon-steel overpack of ~6-in. thickness, as the corrosion rates observed under these conditions are <1 in./1000 yr. These data, for "anoxic" and "oxic" test conditions, are summarized in Table 3.2. The low-oxygen or "anoxic," test conditions, with a dissolved oxygen level in the feed brine of 0.2 ppm, corresponds to low-oxygen conditions that might eventually prevail in a sealed repository; in this test the feed brine is sparged with argon. The high-oxygen level (1.5 ppm) corresponds to the level of dissolved oxygen expected if oxygen at 0.2 atm partial pressure is in equilibrium with the brine. In both cases, the feed brine enters the auto-

clave at 35 mL/hr, on a once-through basis. Both sets of data were obtained at 150°C, considered a reasonable compromise temperature to represent long-term repository characteristics. The tests have run a maximum of 4 months and thus must be considered very short-term by repository standards.

The highest corrosion rates found corresponded to the 1-month exposure to anoxic Permian Basin salt brine No. 1. When the specimens were exposed to Permian Basin salt brine No. 2 (to mitigate feedline plugging during autoclave operation) the rates dropped markedly; also, in the "oxic" study, the rates were considerably less than those

TABLE 3.2. General Corrosion Data Compilation 150°C Brine Studies, PNL, FY 1983

Brine Type	Material	Exposure Time, mo	Penetration Rate, ^(b) Mils/yr (mm/yr)
Anoxic Permian Basin Salt Brine No. 1	2-1/2% Cr, 1% Mo cast steel	1	0.48(0.012), 0.49(0.012) ^(c)
	1025 cast steel	1	0.68(0.017), 0.91(0.023)
	Ductile cast iron	1	0.74(0.019), 0.59(0.015)
Anoxic Permian Basin Salt Brine No. 2	2-1/2% Cr, 1% Mo cast steel	4 ^(a)	0.17(0.0043), 0.15(0.0038)
	1025 cast steel	3	0.20(0.0051), 0.16(0.0041)
	Ductile cast iron	4 ^(a)	0.21(0.0053), 0.15(0.0038)
	1025 wrought steel	3	0.52(0.013), 0.24(0.061) 0.58(0.015)
Oxic Permian Basin Salt Brine No. 2	2-1/2% Cr, 1% Mo cast steel	1	0.11(0.0028), 0.11 (0.0028)
	1025 cast steel	1	0.12(0.0031), 0.13(0.0033)
	Ductile cast iron	1	0.18(0.0046), 0.17(0.0043)

(a) First month's exposure was in anoxic Permian Basin salt brine No. 1 (first three rows of table).

(b) Assuming linear corrosion kinetics.

(c) Replicate specimen data.

observed in the first-month exposure in anoxic Permian Basin salt brine No. 1. Intuitively, as the two brines are so close in composition and (ambient) pH, one would not expect a profound difference in corrosiveness. The level of oxygen in the feed brine, at the levels employed, would be expected to have little or no effect on the corrosion observed. The samples are corroding at rates that are far in excess of the rates of oxygen access to the system, in both the "oxic" and "anoxic" tests, so the corrosion rates do not depend directly on oxygen availability under the conditions studies. On the whole, the corrosion rates found in the non-irradiated brine studies are not overly severe; a corrosion allowance of 1 in. appears adequate for 1000-yr corrosion service. It should be further pointed out that the corrosion found to date has been uniform, with no unusual pitting attack in evidence.

Irradiation-Corrosion Testing. Ferrous materials tested under irradiated-brine conditions showed a considerably higher corrosion rate than those under unirradiated conditions (see Figure 3.1). The penetration data presented, however, were obtained under irradiation dose rate conditions more intense than those expected in a repository at the surface of a thick-walled waste package. The data do, however, give reason for concern and demonstrate a need to clearly define the effects of irradiation on metal corrosion, as the corrosion rates obtained under irradiated-hydrothermal conditions were about tenfold those observed under non-irradiated conditions. Also, specimens from the top of the autoclave clearly showed the highest corrosion rates. This is probably due to a temperature gradient existing in the autoclave: the top was at 150°C and the bottom at 110°C. Advantage was taken of

FIGURE 3.1. Irradiation-Corrosion of Ferrous Materials in Permian Basin Brine No. 2 at 1×10^5 rad/hr and a Maximum Temperature of 150°C

this gradient to obtain an activation energy associated with the observed corrosion rates.

Considering only the 1025 cast and wrought steel specimens, shown in Figure 3.1, upper bounds (150°C) and lower bounds (110°C) on the data points associated with these materials were determined. These rates, along with the corrosion rate of carbon steel in 90°C anoxic simulated seawater irradiated at a dose rate of 1.5×10^5 rad/hr, were plotted against the reciprocal temperature in accordance with findings by G. P. March et al. (1980/1982) (see Figure 3.2). The resulting activation energy, 2600 cal/mole, agrees closely with the activation energies associated with corrosion of steels in the presence of excess oxygen, viz., 2000 to 8000 cal/mole, as reported by H. H. Uhlig (1963), and suggests a corrosion mechanism involving the diffusion of oxidiz-

ing species present in the aqueous environment under conditions of irradiation to cathodic sites on the corroding steel surface.

The effect of irradiation intensity per se on the corrosion rates has not yet been determined. It is reported, however, by March et al. that a dose rate of 3.1×10^3 rad/hr in a simulated seawater environment at 90°C has little effect on corrosion of carbon steels relative to tests performed under unirradiated conditions. Tests of ferrous materials are currently under way at PNL, in Permian Basin brine No. 2 at 150°C and a gamma irradiation intensity of 2×10^3 rad/hr, to determine whether these more relevant dose rates significantly affect corrosion kinetics.

Enviromechanical Studies. Recent efforts in this subtask have emphasized the

FIGURE 3.2. Arrhenius Plot of Irradiation-Corrosion Data, Cast and Wrought Mild Steels in Permian Basin Brine No. 2 (110 and 150°C) and Simulated Seawater (90°C)

slow-strain-rate (SSR) and fatigue-crack-growth rate (FCGR) testing of mild-steel-plate specimens. In an SSR test, a metal specimen is slowly strained to failure in an environment representative of that expected under service conditions. Susceptibility to fracture appears as a diminution of ductility or strength of the material relative to that found in an inert environment. The test is qualitative and is useful for ranking materials or uncovering susceptibilities to stress-corrosion-cracking. FCGR testing is more difficult to perform but, in theory, is capable of providing quantitative data, tying crack motion to a stress intensity near a flaw. The stress intensity is a function of determinable variables, i.e., the load, the flaw size, and the flaw shape.

A wrought 1025 steel specimen was exposed to 150°C Permian Basin brine No. 2 for 2 weeks prior to SSR testing at a relatively high strain rate (10^{-4} in./in.-sec). The purpose of the test was to determine whether the previously observed embrittlement was environmentally induced (e.g., hydrogen embrittlement) or enviromechanically induced (e.g., stress-corrosion cracking). The specimen showed slightly higher ductility than had any of those previously tested. This indicates that the combination of slowly-applied load and the hot brine environment is necessary to cause cracking to occur, so that the diminution in ductility cannot be attributed to hydrogen embrittlement.

To date, the following observations can be made concerning slow-strain-rate test results:

For Ductile Iron

- The ductility of as-cast ductile iron is very low (~4-8% elongation).

- Ductility is lower in Permian Basin salt brine No. 2 than in air at 150°C, and is particularly adversely affected by testing at the lowest strain rates (2×10^{-7} in./in.-sec).

For 2-1/2% Cr, 1% Mo Cast Steel

- There was no difference in ductility measured at relatively high (10^{-4} in./in.-sec) and low (2×10^{-7} in./in.-sec) strain rates in air at 150°C.
- This material was adversely affected by the Permian Basin salt brine No. 2 environment. Reduction of cross-sectional area was lower at strain rates of 10^{-4} in./in.-sec than at 2×10^{-7} in./in.-sec; and both elongation and reduction of area were diminished in the Permian Basin salt brine No. 2 environment. Elongation decreased moderately (by about a quarter), but reduction of area decreased by about half.
- Some superficial surface cracking was observed in the neck region of specimens tested in air as well as those tested in Permian Basin salt brine No. 2. In addition, brine specimens were deeply cracked, particularly those tested at the lowest strain rates; this probably contributed to elongation of the specimens. These fracture surfaces were predominant ductile, with some evidence of secondary cracking. Portions of the cracks in the neck region appeared distinctly intergranular.

For Wrought 1025 Steel Plate

- Ductility was slightly diminished by testing at low strain rates (2×10^{-7} in./in.-sec) in air at 150°C.
- Ductility was not affected by Permian Basin salt brine No. 2 relative to air at strain rates of 10^{-4} in./in.-sec.

- Surface roughness was found in the neck region of specimens tested in brine. Surface cracks were present in specimens tested at the lowest strain rate. These cracks did not have the depth or intergranular appearance of those found on the 2 1/2% Cr, 1% Mo specimens.

An FCGR test of wrought 1025 steel plate in deionized water was completed in May. Data from the FCGR test was evaluated using three techniques for determining specimen compliance. The resultant crack-length vs cycles data are being analyzed using statistical methods to determine the optimum method of reducing and evaluating FCGR data from specimen compliance measurements.

Glass Interactions

Glass leaching in saturated Permian Basin salt brine No. 1 was generally slower than

in deionized water. Differences in rates were most pronounced at relatively high values of the product of the glass surface area to solution volume ratio (SA/V) and time, as shown in Figure 3.3 for silicon dissolution from 76-68 glass at 90°C. For relatively high values of SA/V x time, this plot reflects the difference in solubility of silicon in the two solutions. For relatively low values of SA/V x time, where solubility effects should be unimportant, dissolution in the two solutions is similar. These results are consistent with earlier findings in this program that glass leaching in silicic acid solutions decreased substantially with increasing silicon concentration. It is this dependence of glass leaching rates on silicon solution concentrations that is responsible for the generation of smooth curves in plots of concentration versus SA/V x time.

FIGURE 3.3. Log Silicon Solution Concentration Released from 76-68 Glass as a Function of the Log of the Product of Surface Area to Solution Volume Ratio and Time

The presence of ductile iron in the container significantly increases the leaching rate of 76-68 glass. A comparison of boron dissolution from this glass versus SA/V x time at 50, 70, 90, and 150°C is given in Figures 3.4a and 3.4b for glass alone and with iron. Boron concentrations are illustrated because boron does not readily form compounds or sorb under these experimental conditions and, therefore, can be used to indicate glass reaction. Leaching rate enhancements are most significant at relatively high values of SA/V x time, where boron release at 70°C with ductile iron actually exceeds that of glass alone at 150°C. These results are an extension of earlier findings of this program where ductile iron was found to accelerate glass corrosion in deionized water as well as in several ground waters. The mechanism by which iron accelerates leaching is thought to involve iron-silicate colloid formation,

which reduces the activity of silicon in solution and, thus, the saturation fraction. Curvature in the plots of dissolution versus SA/V x time is shown in Figure 3.4a for glass alone. Increased by saturation effects, curvature is lessened by the presence of ductile iron, especially at high values of SA/V x time. Of course, the acceleration in leaching due to ductile iron is dependent upon the surface area of iron exposed to the leachant.

Gamma radiolysis of deaerated Permian Basin salt brine No. 1 leads to an increase in the leaching rate of 76-68 glass. Rate enhancements are most obvious at 50°C, as shown in Figure 3.5, but are unimportant at 90°C, as shown in Figure 3.6. These findings agree with our earlier studies in deionized water, where the importance of radiolysis to glass leaching decreased with increasing temperature. It was concluded previously that the enhanced leaching is due

FIGURE 3.4a. Log Boron Solution Concentration Released from 76-68 Glass as a Function of the Log of the Product of Glass Surface Area to Solution Volume Ratio and Time

FIGURE 3.4b. Log Boron Solution Concentration Release from 76-68 Glass Plus Ductile Iron as a Function of the Product of Glass Surface Area to Solution Volume Ratio and Time

FIGURE 3.5. Log Boron Solution Concentration Released from 76-68 Glass, 76-68 Glass plus Ductile Iron, with and Without Gamma Irradiation, as a Function of the Product of Glass Surface Area to Solution Volume Ratio and Time at 50°C

FIGURE 3.6. Log Boron Solution Concentration Released from 76-68 Glass, 76-68 Glass plus Ductile Iron, with and Without Gamma Irradiation, as a Function of the Product of Glass Surface Area to Solution Volume Ratio and Time at 90°C

to the generation of free radical species such as the hydroxyl radical. These species are already in an excited state such that an increase in temperature from 50°C to 90°C would not significantly increase their reactivity. Thus leach rate enhancements due to radiolysis appeared to be temperature independent. Since normal corrosion of glass increases with increasing temperature, effects due to radiolysis become proportionally less important.

Actinide solubility studies in Permian Basin brine No. 1 have been started using actinide-doped 76-68 glass. The solubilities of Pu, Np, and Am are being considered. Currently Am solubility at 25°C has been evaluated in fully concentrated brine, in a 10X diluted brine, and in deionized water. Within experimental error, the solubility values are the same in all three solutions. This is both surprising and significant. If

this relationship holds for other actinides and under varying conditions of temperature and chemical environment, then solubilities of actinide compounds in salt brines can be obtained, to a large degree, from existing literature.

Interactive tests involving actinide-doped 76-68 glass and ductile iron have been completed in 90°C brine. Preliminary results indicate that although glass/brine interaction is enhanced in the presence of iron (as was observed in nonradioactive glass), the amount of actinides in solution after filtration is less. This is because actinides are sorbed on the iron and the precipitates. Therefore, if the effect of colloids can be neglected, then iron is beneficial because by scavenging it reduces the amount of actinides available for release from the waste package.

Spent Fuel Interactions. Spent fuel interaction tests have taken a two-pronged approach. An initial series of interaction tests between unclad spent fuel and iron in Permian Basin brine No. 1 has been completed. These tests were conducted at both 25 and 75°C for times up to 60 days. A second series of interactive tests involving unirradiated UO₂ fuel pellets, iron, and oxidized zircaloy cladding material has been completed under identical conditions as the initial spent fuel experiments. The experiments involving UO₂ will allow more analytical tests to be utilized, and a better understanding should allow a more meaningful test matrix to be designed for interactive experiments with clad spent fuel.

Colloid Investigations. This research is for determining the impact of colloids on release from the repository. As such, the formation, stability, characterization, and radionuclide sorption/desorption characteristics of colloids will be investigated.

In our first series of tests, colloid formation resulting from exposing various ratios of iron and glass to Permian Basin brine No. 1 has been evaluated at 90°C for times to 60 days. More colloids form as the ratio of iron to glass surface area increases. At 60 days exposure time, the colloid sizes are predominantly greater than 0.1 micron. However, a small fraction (<1%) of the colloids appears to be smaller. These results are based upon filtration experiments, and more sophisticated techniques are required for better size distribution analyses. These techniques, such as hydrodynamic chromatography, will be available for sample analysis by October 1983.

In addition to colloids that form due to the presence of both iron and glass, they also form when only actinide-doped glass is present. The iron silicate colloids are most numerous and represent the class of pseudo colloids. However, true colloids are actinide colloids such as hydroxides, etc., and represent colloids with high transport potential. The actinide-doped glass leaching experiments have shown the development of significant quantities of actinide-containing true colloids. These are observed both by light-scattering experiments and filtration.

Brine Radiolysis. If brine migrates into the repository during the thermal pulse period, it will be exposed to gamma irradiation. After the canister is breached, brine will be exposed to alpha radiation. Therefore, an understanding of the behavior of brine in both an alpha and a gamma irradiation field becomes important. Results are reported here on redox potentials found during alpha irradiation as well as gas pressures generated by different salt solutions during gamma irradiation.

Alpha Radiolysis Results. Relatively low redox potentials are expected under the repository conditions. However, due to radiolytic effects, redox conditions near the waste package may be different than in the host-rock environment. Therefore, the effect of alpha radiation on the redox conditions (represented by pe, which is equal to 16.9 times Eh in volts) was determined.

Aliquots of Permian Basin brine No. 1 were degassed with N₂, spiked with ²⁴⁴Cm to obtain 1.5 x 10⁻⁵ to 3.7 x 10⁻⁶ M Cm, and equilibrated in sealed quartz vessels (suitable to pressures of 3 atm) for ~40 days at

25°C. These conditions represented a range in total dose of $\sim 9.1 \times 10^5$ to 3.7×10^6 rads/aliquot. Both the aqueous and the gaseous phases were analyzed.

The results presented in Figure 3.7 show that at the highest Cm concentration the pH of the brine solutions decreased to as low as 2.4. The pe values, as measured with a combination platinum electrode, increased to about 20. The gaseous and aqueous phase analyses (production of NO_2^- , O_2 , H_2O_2) qualitatively support the measured redox potentials. These measured redox potentials (Figure 3.7) are extremely oxidizing, fall outside the water stability field, and indicate that highly oxidizing conditions may exist near the waste-water interface.

As a result the solubility of tetravalent actinide compounds (such as NpO_2 and PuO_2 , which may be present in the waste) is expected to be higher than at the host-rock redox conditions. It should be noted that the gas phase composition was the same for both alpha and gamma radiolysis, roughly 75% H_2 and 25% O_2 .

Gamma Radiolysis Results.

Figures 3.8 and 3.9 show total gas pressure generated as a function of normalized dose (gigarads) in a cobalt-60 irradiation facility. The dose was normalized by multiplying the dose by the ratio of liquid volume to gas plenum volume. This ratio was typically in the range of 3 to 5. The solutions were

FIGURE 3.7. Effect of Alpha Radiation on pH and pe of Permian Basin Brine and Its Comparison with the Estimated Range in pe-pH of Salt Repository Environment. Dashed lines represent the upper and lower stability limits of water. Approximate natural limits of Eh and pH of aqueous environments are shown by solid lines.

FIGURE 3.8. Pressure Generated by Gamma Radiolysis of Salt Solutions

FIGURE 3.9. Pressure Generated by Gamma Radiolysis of Permian Basin Brine

irradiated at about 75°C in sealed stainless steel vessels with quartz liners to prevent contact between the stainless steel and the solution. The gas plenum originally contained air at atmospheric pressure. The resulting gas composition (from the original air) was found to be roughly 75% H₂ and 25% O₂.

Data presented last quarter showed that the equilibrium gas pressure generated by synthetic Permian Basin brine No. 1 was about 100 atm. Solutions containing Cl⁻, Br⁻, or both had lower equilibrium pressures, demonstrating that at least one more anion must be included to simulate the Permian Basin brine.

Figure 3.8 shows the Permian Basin brine data and also presents data on solutions containing SO₄⁼. The anion concentrations in all cases were the same as in the brine; the cation in these solutions was Na⁺. It is clear that the three anions, Cl⁻, Br⁻, and SO₄⁼, are both necessary and sufficient to simulate the pressure generated by the Permian Basin brine No. 1. It is also clear from these data, together with those presented last quarter, that there is some synergism between these ions; but the mechanism of this synergism has not been determined.

Figure 3.9 shows pressure-generation curves for Permian Basin brine No. 1 alone, and for that brine plus solid ductile iron, and for that brine plus undissolved Permian Basin salt. If the solid salt were effectively inert, then the dose normalization calculation should cause the pressure curve to fall on top of the curve for brine alone. Figure 3.9 shows that this is, in fact, the case. The presence of ductile iron (chunks with total surface area of 11.2 cm² compared with a solution volume of 17.0 cm³) caused a

somewhat slower pressure buildup and a lower equilibrium pressure than in the brine.

Crystalline Salt Radiolysis. This new subtask is evaluating potential changes in the chemical environment of a nuclear waste repository in salt due to crystalline salt radiolysis. Gamma irradiation of alkali halides is well known to yield two principal defects: 1) F-centers (an anion vacancy containing a trapped electron) and 2) H-centers (interstitial halogen atoms). The F-centers may coalesce into alkali metal colloidal particles, imparting a blue color to the irradiated crystal. However, it is the fate of the interstitial halogens that is most critical when assessing the potential impact of radiolysis on the chemical environment of the waste package. With sodium chloride, if chemical chlorine can be lost from the irradiated salt, dissolution of the remaining solid will result in highly basic solutions, and, of course, there are hazards associated with free chlorine. If no chlorine can be lost, solutions will be approximately neutral. From the series of dissolution and crushing/annealing experiments performed to date, it has not been possible to release a significant fraction of the chlorine held as H-centers from either NaCl or from natural rock salts from the Permian Basin.

The concentration of radiation-induced defects in the Permian Basin rock salt was consistently five times greater than observed for NaCl for the same total dose, as evidenced by the OCl⁻ solution concentration upon dissolution. These results are not unexpected since it is well known that alkaline earth cations can stabilize radiation-induced defect centers in NaCl. For the Permian Basin rock salt, the highest defect

concentration actually measured was 0.13 mole percent, while that for NaCl was 0.026 mole percent at a total dose of 5×10^9 rad for the rock salt. If no chlorine is lost, the pH of the solution will be controlled by OCl^- in the short term and should not exceed 10 for a total dose of 5×10^{10} . Following disproportionation of OCl^- to ClO_3^- the solution should be neutral. However, if all the chlorine held as H-Centers were to escape, the solution pH should be about 13. Bounds of the pH as a function of total dose are shown in Figure 3.10 and are based upon the stored energy/ OCl^-/H_2 data of Jenks, et al. (1975, 1977). Others (Levy 1983) claim that damage increases faster than a linear dependence upon dose, so that effects might be more than ten times the present estimate.

Solution pH values upon dissolution of irradiated NaCl generally exceeded that of the rock salt for the same total dose. This occurred despite greater defect production for the rock salt as evidenced by OCl^- solution concentrations. For NaCl, the measured pH (corrected by +0.6 units for salt error) agreed reasonably well with that predicted for pH control by OCl^- , while that for the rock salt was about one unit smaller than expected from OCl^- concentrations. Lack of agreement in the case of the rock salt is probably due to some buffering action by sulfate and carbonate, which are contained in the rock salt but not in NaCl.

To date, dissolution of irradiated Permian Basin rock salt and NaCl has not yielded major changes in the chemistry of

FIGURE 3.10. Solution pH Versus Log Total Dose Considering (A) Loss of All Chlorine Held as H-centers, (B) No Loss of Chlorine and pH Control by OCl^- , and (C) All OCl^- Disproportionates to ClO_3^- . Curves were calculated from the stored energy data of Jenks et al. (1975).

the solutions. It has not been possible so far to remove a significant fraction of chlorine held as H-centers from the irradiated salts using any combination of crushing and annealing. However, it is essential to analyze salts actually irradiated in the 10^{10} rad range to avoid uncertainties associated with extrapolation to that dose. Future work will concentrate on polycrystalline rather than powdered material.

Component Compatibility

Hydrothermal Testing of Package Components in Salt. Dickson direct-sampling rocking autoclaves are being used in our effort to determine the chemistry of Permian Basin salt brine No. 1 as a function of temperature. These autoclaves presently offer the best means of taking solution samples without the possible problems caused by quench-phase formation during the time needed to cool a standard autoclave for taking samples.

In the tests with 76-68 glass in brine at 150 and 250°C (Figures 3.11 and 3.12), the concentrations of Ca^{2+} in solution drop to approximately the values expected in brine alone as a result of inverse solubilities (970 ± 28 g/mL at 150°C and 670 ± 44 g/mL at 250°C), indicating no significant interaction with the glass. Concentrations of Mg^{2+} in the brines, however, drop considerably below the values expected on the basis of inverse solubility alone (128 ± 3 mg/L at 150°C and 51 ± 20 mg/L at 250°C), indicating considerable reaction with the glass.

Components leached from the glass (barium, boron, silicon, and zinc) show the expected rapid increase with time, the rates of increase being somewhat more rapid in the test at 250°C. In tests both at 150 and

250°C, the zinc concentrations rise through a maximum and then decrease to values in the range of 50 to 60 mg/L, explainable perhaps by the formation of a crystalline zinc phase similar to those described from low-temperature tests. An interesting feature of the glass component curves for the 250°C test is the increase in slope exhibited between 40 and 50 days. This increased leach rate indicates that the early flattening of the curves is not a result of solubility control, but of another mechanism, possibly formation of a crystalline protective layer. The increase in leach rates between 40 and 50 days could then be a result of breakdown or spalling of the protective layer, possibly as a result of the mechanical agitation caused by the rocking motion of the autoclave. Detailed characterization of solids from static autoclave tests under the same conditions should help resolve this issue.

Iron leached from 76-68 glass shows very similar behavior in both the 150°C and the 250°C tests, rising rapidly to >10 mg/L and then decreasing to a much lower value (4-5 mg/L at 150°C, <1 mg/L) at 250°C. A colloidal formation mechanism incorporating iron is probably at work in the tests with 76-68 glass; however, in this case the colloids may well be iron silicates, as observed at lower temperature tests with 76-68 glass, rather than iron oxides.

The tests described above were carried out at 150 and 250°C with Permian Basin salt brine No. 1 which is saturated with NaCl at 25°C. Dickson autoclave tests have not yet been carried out with brines that are saturated at the temperature of the test; therefore, to assess the effect of brine strength upon glass behavior, we have carried out a short-term Dickson autoclave test with half-strength Permian Basin salt brine No. 1. In

FIGURE 3.11. Plot of Solution Composition (mg/L) as a Function of Time (days) for Permian Basin Brine No. 1 in Contact with 76-68 Glass at 150°C and 20 MPa. Initial SA/V = 10 m^{-1} .

this test calcium does not decrease at all and magnesium decreases much as it does in full-strength brine tests. The shapes of the glass component curves (silicon, boron, zinc, and barium) are similar to those in the tests with full-strength brine; however,

the concentration values attained over equal time periods are considerably lower, indicating that decreased brine strength decreases degradation rate of the glass.

The relative concentrations of boron and silicon in the tests with 76-68 glass in

FIGURE 3.12. Plot of Solution Composition (mg/L) as a Function of Time (days) for Permian Basin Brine No. 1 in Contact with 76-68 Glass at 250°C and 20 MPa. Initial SA/V = 10 m⁻¹.

brine are interesting and may indicate the formation of a boron phase in some of these tests. Reconnaissance tests with MgCl₂-rich brine and 76-68 glass (1 to 2 weeks in cold-seal pressure vessels) at 300 and 400°C indicate (through x-ray diffraction analysis of solid test products) that the rare earth borosilicate mineral stillwellite [(Ce,Lu)BSiO₅] forms from the borosilicate

glass under these conditions. It seems quite possible that stillwellite or a similar phase forming in smaller quantities may help explain the observed variations in boron concentrations.

Testing in Dickson direct-sampling autoclaves to determine the solubility of uranium in deionized water and Permian Basin brine No. 1 at 150°C (20 MPa) was concluded

after durations between 1 and 2 months. These tests, carried out with thin slabs of polycrystalline UO_2 (depleted) cut from sintered pellets (>95% TD), were intended to help provide a data base for interpreting future tests with spent fuel. About 20 thin UO_2 slabs were used in each test to give a SA/V ratio of 10 m^{-1} . Uranium concentrations were determined by laser fluorescence calorimetry.

Uranium concentrations in both 0.45- μm and 15- $\text{\AA}$ filtrates, as a function of test duration, for deionized water and Permian Basin brine No. 1 are presented in Figure 3.13. As can be seen, concentrations in all four data sets pass through a maximum after about 11 days at temperature and then decrease somewhat more slowly, reaching values near or below 0.1 mg/L after ~40 days. The most likely explanation for this behavior is the early dissolution of UO_2 followed by the nucleation and growth of one or more new uranium compounds, possibly hydrous uranium oxides with lower solubilities. The similarity of the uranium concentrations after 1 month may indicate that similar solid phases are controlling the final solubility of uranium in both the deionized water and the brine systems. The pH of deionized water and brine changed as a function of time; from starting at 7 and 5 for brine and deionized water, respectively, the brine pH went through a minimum and the deionized water a maximum of 1.5 pH units at about the time corresponding to the uranium concentration maximum. After that the pH of both solutions returned to their initial values.

Dickson autoclave tests have been started to determine the solubility of amorphous silica in Permian Basin brine No. 1. These data will be very useful in interpreting

leaching data for 76-68 glass in the brine and in determining whether or not silica solubility plays a major role in controlling glass leaching at high temperatures.

Work has also been initiated to determine brine compositions resulting from the dissolution of Permian Basin, Lower San Andreas Unit #5 salt and Paradox Basin salt cores. Work has also been started to determine whether or not inclusion brine can be separated from salt core material through the use of an organic solvent that is immiscible with water.

Autoclave System Modification. The two autoclaves from the hot cell (19 liter) autoclave system have been sent out for final modifications. These modifications should be completed during August 1983, and the autoclave system should be moved into the 324 Building hot cell area by the end of FY 1983.

LLNL Beach Leach II Experiment. All counting activity for both solids and liquids for the test, except for the XRF determination of solution uranium concentrations, has been completed. A final data report is to be issued before the end of FY 1983.

Modeling

Corrosion Modeling Task - Radiolysis.

The corrosion of iron overpack materials for nuclear waste forms in salt is highly dependent upon the species produced by radiolysis of brines which contact the metal. A computer code has been developed that attempts to predict the concentrations of the radiolytically produced species in a brine as a function of time using published

FIGURE 3.13. Plot of Uranium Concentrations (mg/L) Versus Test Duration (days) for Dickson Autoclave Tests with Sintered UO_2 in Deionized Water (DIW) and Permian Basin Brine No. 1 (PBB1)

values for radiation yields of species and chemical reaction rates.

Radiation interacts with brines through ionization and excitation of water molecules. The excited water molecules then decompose into several new species:

The number of each species produced, or destroyed, per 100 eV of energy deposited is known as the G value. The G values are shown in Table 3.3 (Burns et al. 1983) for gamma and alpha radiations.

TABLE 3.3. Primary Radiolytic Species G Values for Gamma Radiation

Species	H ⁺	e _{aq} ⁻	H	OH	HO ₂	H ₂	H ₂ O ₂	H ₂ O
Gamma	2.7	2.7	0.61	2.86	0.03	0.43	0.61	-4.14
5 MeV alpha	0.3	0.3	0.3	0.5	0.10	1.4	1.3	-3.3

After the new species are produced, they are free to interact with the constituents of the brine via a series of chemical reactions (34 reactions are used for the analysis of a NaCl brine). Using the theory of first-order chemical reaction kinetics and the G values, a system of differential equations describing the rate of change of various species in brines is developed:

$$\frac{\partial C_i}{\partial t} = G_i D + \sum_{r=1}^{\text{NRTN}} m_{ir} k_r$$

$$\sum_{j=1}^{\text{NSPEC}} (C_j) |m_{jr}|, i = 1 \text{ to NSPEC}$$

$m_{jr} < 0$

C_i = concentration of i th species.

G_i = radiation yield of i th species.

D = dose rate.

NRTN = total number of chemical reactions.

SPEC = total number of species considered.

$m_{(i \text{ or } j)r}$ = stoichiometric coefficient of the i th species in the r th chemical reaction (if i th species is a reactant, $m_{ir} < 0$; product, $m_{ir} > 0$; nonparticipant, $m_{ir} = 0$).

k_r = rate constant for r th reaction.

A computer code, RADIOL, sets up and evaluates the above system of equations using a computer routine, LSODES, which solves stiff nonlinear ordinary differential equations (Hindmarsh).

RADIOL has been used to evaluate the effects of radiolysis on brine solutions. The brines of importance to the ONWI program are high in NaCl with several minor constituents, ex. SO_4^{2-} , Br^- , K^+ , Mg^{++} . To date, results are only for a pure concentrated NaCl brine, with no nitrogen in the gas phase.

The reaction sequence input to RADIOL for the pure NaCl brine includes the reactions given by Burns et al. as well as an overall reaction representing the interaction of the chloride radical, $\text{Cl}^\cdot$, with water:

which has been given a speculative rate constant of $1.0\text{E}9 \text{ mole}^{-1}\text{s}^{-1}$.

Typical results from RADIOL for a 5.3 M brine is given in Figure 3.14. The activation energies for most of the reactions are equivalent; therefore temperature has virtually no effect upon the species concentrations.

Dose rate is shown to have the most profound effect upon the concentrations. An increase to twice the dose rate shows a proportional increase in the concentrations of H_2 , e^- , H_2O_2 , OH , HO_2 , and HO_2^- . The pH was lowered, due to equilibration with O_2 , by somewhat less than two units. Chloride radical initially is increased proportionally to the square root of the dose rate change due to the second-order reaction with water.

The effect of initial oxygen concentration was confined to the radical species H and e^- with the following approximate dependencies on oxygen and dose:

FIGURE 3.14. Plot of Radiolytically Produced Species Concentrations Versus Time as Predicted by the Computer Code RADIOL at a Dose Rate of 5 M rad/hr and an Initial Oxygen Concentration of 1.5 ppm.

$$[H] = \frac{G(H) \cdot D}{I [O_2]} \quad k = 1.90E10 \text{ mole}^{-1} \text{ s}^{-1}$$

and

$$[e^-] = \frac{G(e^-) \cdot D}{k [O_2]} \quad k = 1.3E10 \text{ mole}^{-1} \text{ s}^{-1}$$

After a period of time (dependent upon dose rate) the concentration of H_2O_2 will begin to dictate some of the equilibrium species concentrations:

$$[Cl] = \frac{G(OH) \cdot D}{k [H_2O_2]} \quad k = 5.0E9 \text{ moles}^{-1} \text{ s}^{-1}$$

Hence, H , e^- , and Cl are examples of species whose concentrations are proportional to D .

The equilibrium values for the gas-phase constituents H_2 and O_2 have not been established yet. Work will continue to improve the code RADIOL and to evaluate the gas constituents.

Spent Fuel Leach Modeling. The objective of this subtask is to develop a model to describe the leaching of spent fuel. The approach is to review the literature for models for the rate of dissolution of UO_2

and for results of actual leach tests of spent fuel. The information is then used to formulate a description of the leaching process. Based on this description, changes will be suggested for ONWI's Waste Package Performance Assessment Code (WAPPA).

Five sources of spent fuel leaching data useful for our purposes have been identified and reviewed. Included is work performed in Sweden and Canada and work in the USA by PNL, LANL, and ORNL. The data from Canada, LANL and PNL are particularly applicable to the present study. The tests typically followed an IAEA procedure (leachant replaced periodically), although one series of tests at PNL followed a static test procedure (leachant not replaced). While several different leachants were used in the tests, we looked specifically at results of tests in deionized water and in salt brines. We also looked only at the releases of uranium, cesium, strontium, europium, and cerium.

Based on the available data, it appears that the leaching of spent fuel can be described as oxidation of the UO_2 matrix resulting in congruent release of fission products and actinides. There may be an initial period of rapid release of cesium due to its high concentration at the fuel/cladding interface.

Brine Chemistry Review. The rate of corrosion of structural barriers and the rate of release of radionuclides from a waste package depend in various ways on the chemical environment provided by heated brine. To predict the effect of this environment and to extrapolate from laboratory experiments to the repository environment, it is important to improve our understanding of activity coefficients and pH values in brines. To this end, a literature review

has been undertaken to assist with the interpretation and modeling of experimental data.

Individual Ion Activity Coefficients.

Individual ion activity coefficients cannot be measured experimentally (or calculated from experimental data using an ion-associated approach) without making non-thermodynamic assumptions. Several different approaches have been used, as follows.

Bates et al. (1970) describe how hydration theory can be extended to calculate single-ion activity coefficients for unassociated chlorides. Their assumption (convention) is that the chloride ion is not hydrated. Values of individual ion activity coefficients (molal scale) using this method are tabulated in the reference, based on the univalent chlorides HCl, LiCl, NaCl, KCl, RbCl, CsCl, and NH_4Cl , and the divalent chlorides $MgCl_2$, $CaCl_2$, and $BaCl_2$.

Truesdell and Jones (1974) used both an extended Debye-Hückel equation and the mean salt method (using the MacInnes assumption) to calculate individual ion activity coefficients and compared these values to those calculated using the Stokes-Robinson hydration theory (Bates et al. 1970). The MacInnes assumption is that $\gamma_{\pm KCl} = \gamma_{K^+} = \gamma_{Cl^-}$ as an approximation, where these are the activity coefficients for the cation, anion, and neutral salt in this case. In general, the symbols would be $\gamma_{\pm}$, γ_+ , and γ_- . Using the mean salt method outlined in Garrels and Christ (1965), one can calculate values of individual ion activity coefficients using data for $\gamma_{\pm KCl}$ and $\gamma_{\pm}$ for another solute.

Equations can also be written and solved for single-ion activity coefficients of anions. An additional assumption made by

Truesdell and Jones (1974) is that activity coefficients in simple solutions equal those in multicomponent solutions of the same ionic strength. They mention further that this assumption is reasonable for dilute solutions, but may not hold for more concentrated solutions (>1.0 mole). In the reference, single ion activity coefficients are calculated for Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , and CO_3^{2-} .

Whitfield (1975) has also calculated values for individual ion activity coefficients for seawater constituents (including trace constituents) at 25°C using the Bronsted-Guggenheim equations. The calculations are based on a model "recipe" for a seawater composition at an ionic strength of 0.7 mole, and the assumption was made that the bulk composition remained constant for his calculations of γ_+ and γ_- out to 3.0 mole. He also performed the same

calculations using Pitzer and co-workers' equations, but the agreement between the two methods is quite good and reproduction of this second calculation would be redundant.

Unfortunately, similar sets of data have not been located for γ_+ and γ_- at elevated temperatures. In general, based on the data seen for γ_+ of strong electrolytes (unassociated), γ_+ values decrease with increasing temperature (e.g., NaCl). Data at elevated temperatures are scarce except for a few common solutes. At first glance, there seems to be no reason why this approach (ion-interaction) used by either Whitfield or Pitzer and co-workers cannot be used at higher temperatures provided the data for γ_+ of solutes of interest are available.

The single ion activity coefficients calculated in the references cited are summarized in Table 3.4 for the ions Mg^{2+} and SO_4^{2-} . These ions are particularly

TABLE 3.4. Summary of Calculated Single-Ion Activity Coefficients from the Literature Cited. $T = 25^\circ\text{C}$

Molality	Mg^{2+}					SO_4^{2-}		
	DH	MS	SR	W	B	DH	MS	W
0.1	.406	.400	.390		.279	.371	.368	
0.2				.301	.239			.244
0.4				.247				.174
0.5	.292	.289	.247		.234	.205	.214	
0.6				.224				.140
0.7				.217				.128
0.8				.213				.118
1.0	.297	.293	.230	.207	.344	.155	.155	.103
2.0	.389	.380	.265	.219	1.439	.112	.091	.064
3.0	.554	.567	.350	.271		.091	.085	.047
4.0	.882	.945	.470			.077	.077	

DH = Truesdell and Jones (1980); Extended Debye-Hückel equation

MS = Truesdell and Jones (1980); Mean salt method

SR = Truesdell and Jones (1980); Stokes-Robinson method

W = Whitfield (1975)

B = Bates et al. (1970)

important to understanding pH changes in brines, as is discussed below. The agreement among the methods is not bad at 1.0 mole, but apparently the discrepancies at ~5 mole (i.e., Permian Basin brine) may be significant. Therefore, there is an incentive to study that regime experimentally.

Brine pH Versus Temperature. There is a paucity of experimental data in which changes of pH in brines have been measured as a function of temperature. Only one reference (Bodine 1976) has been located that discusses possible controlling mechanisms of pH. Bodine describes a succession of brines formed by evaporation of seawater in which the pH of the solution decreases with increased evaporation at 25°C from about 8.2 to 6.6. He states that during progressive evaporation of seawater, the brine may become saturated with a magnesium hydroxylchloride salt that incorporates OH⁻ into its structure, resulting in a pH decrease of the brine. Bodine states that this salt has not been identified in natural salt deposits, but also presents some experimental data in which a 3:1 hydroxylchloride tetrahydrate, $Mg_2(OH)_3 Cl \cdot 4H_2O$ was identified by X-ray diffraction, the result of reacting $Mg(OH)_2$ with a 2M $MgCl_2$ solution.

Experimental data relating brine pH changes with temperature that we have been able to locate have involved exclusively the reaction of seawater with various basic and intermediate rocks (e.g., basalt, peridotite, andesite, etc.). It should be emphasized that many of these studies were not designed to specifically determine a change in pH; however pH values (obtained at 25°C) of the solutions are usually reported. Several researchers have also simply heated seawater to temperatures near 350°C, sampled

the fluid at the P-T conditions of the experiment, and measured pH at ambient temperature.

Bischoff and Seyfried (1978) reported geochemical results for the isobaric (500 bars) heating of seawater in the range of ambient to 350°C. They were able to sample solutions at temperature and measure the pH (at room temperature) as well as determine the solution chemistry.

A brief summary of their conclusions is as follows:

- Between 150°C-200°C, anhydrite ($CaSO_4$) precipitates.
- The pH decrease from 7.6 at 25°C to 5.8 at 250°C (and the CO_2 increase) was caused by oxidation of dissolved organic matter.
- The pH decrease between 300°-350°C was caused by precipitation of phase(s) containing Mg, Ca, SO_4 , and OH.

In a separate set of experiments, Bischoff and Seyfried (1978) recovered the precipitates that are stable in seawater at 325°C and identified anhydrite ($CaSO_4$) and a magnesium hydroxide sulfate. They obtained a single crystal X-ray diffraction pattern of this Mg-compound but could not match the pattern with known compounds in the literature.

Since the paper of Bischoff and Seyfried (1978), magnesium-hydroxysulfate-hydrate (MHS_H) has received considerable attention. In a more recent paper (Bischoff and Rosenbauer, 1983), experiments similar to those of Bischoff and Seyfried (1978) were conducted at even higher temperatures using two different fluids. One fluid was a natural seawater; the other, a synthetic "evolved" seawater that has Na, K, Cl concentrations similar to natural seawater, an elevated Ca concentration, a depleted Mg

concentration, and no SO_4 . The results of heating these solutions to $\sim 500^\circ\text{C}$, 1 kb were that the "evolved" seawater, which was initially depleted in Mg and SO_4 , showed very small changes in pH relative to the natural seawater. Using mass balance calculations similar to Bischoff and Seyfried (1978), anhydrite and MSH were identified as precipitates in the natural seawater samples. Furthermore, they reported the stoichiometry of MSH to be $\text{MgSO}_4 \cdot 1/4\text{Mg}(\text{OH})_2 \cdot 1/2\text{H}_2\text{O}$.

Further calculations of Bischoff and Rosenbauer (1983) suggest:

- Neither anhydrite or MSH precipitated during the heating of the Mg- SO_4 depleted solution.
- The pH decrease between 350° - 400°C may be caused by the precipitation of $\text{Ca}(\text{OH})_2$.

However, the amount of Ca lost from solution which would account for this pH change was below the precision of their chemical analyses.

Another possible mechanism of pH reduction in high-ionic-strength solutions (such as seawater) that has a bearing on brine/waste form interactions involves the precipitation of Mg from solution along with excess SiO_2 dissolved from a co-existing solid. As a consequence, H^+ in solution increases to maintain charge balance (Janecky 1982). This parallels work in the Waste Package Program in which talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$] and/or sepiolite [$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$] were identified as products from the reaction of 76-68 glass and Permian Basin brine No. 1. In numerous studies on seawater/rock interactions, similar results have been reported. Some Mg-phases that have been identified in these studies include: talc, sepiolite, chlorite, brucite, serpentine, and Mg-montmorillonite.

Bischoff and Seyfried (1978) state that although the in situ pH (at temperature) is probably different than the quench pH values reported, their data suggest that ionizable hydrogen is being produced at high temperature. Moreover, they concluded that although a change in the distribution of dissolved species at high temperatures could result in a higher H^+ activity, a reversible change in speciation distribution would occur on the quench and the pH of the seawater would be the same before and after heating. Therefore, the decrease in pH noted in their experiments was postulated to be caused by the precipitation of a solid.

In summary, from the literature it appears that three different magnesium precipitates, an oxychloride, a hydroxysulfate-hydrate, and a silicate could potentially cause decreases in pH in heated brines. This shows the importance of characterizing the Mg^{2+} concentration in brines or brine inclusions, and suggests that the precipitates be searched for subsequent to hydrothermal tests with brines.

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3.1.2 Baselining and Benchmarking Salt Performance Assessment Codes (DB-30-30-01 - 80748)

The objective of this program is to provide ONWI with salt site-specific, baselined and benchmarked performance analysis codes to perform the comprehensive analysis required to site, design, and license a repository in salt. Codes to be baselined and benchmarked include SWENT, CFEST, and FE3DGW.

Summary

To site, design, and license a repository in salt ONWI will be required (by NRC regulations as well as good scientific practice) to have salt site-specific baselined and benchmarked hydrologic system performance analysis codes. This year's accomplishments discussed here include:

1. Converting the FE3DGW and CFEST codes from their PDP-11/70 format into large mainframe format to facilitate transfer to other computer systems. This conversion was performed on the PNL VAX 11/780, which is compatible with the ONWI computer system.
2. Making the SWENT code operational on the VAX 11/780.
3. Selecting analytical solutions and collecting codes for these analytical solutions to provide suitable test problems for baselining (i.e. verifying) the

FE3DGW, CFEST, and SWENT finite-element and finite-difference codes for hydrologic flow, heat and solute (brine) transport.

4. Baseline CFEST and FE3DGW against these analytical solutions.
5. Developing salt site-specific hydrologic flow, coupled flow and heat transport, and coupled flow and brine transport benchmark problems.
6. Performing the hydrologic benchmarking of CFEST, FE3DGW and SWENT.

The baseline problems suggested for verification of the SWENT, CFEST, and FE3DGW computer codes were selected from a variety of available analytical and semi-analytical solutions. Analytical solutions to the fundamental ground-water flow equation are exact solutions used in formulating and implementing ground-water models. An analytical solution is a functional expression comprising well-defined elementary mathematical functions and displays the explicit dependence of a physical-state variable on the system parameters and on the spatial and temporal variables. The analytical solutions presented satisfy the fundamental partial differential equations for water movement in a porous media, while constrained to certain initial and boundary conditions. Ideally, an analytical solution is a closed-form expression (i.e., a finite number of mathematical operations involving elementary functions). Certain semi-analytical solutions consisting of an infinite number of operations (infinite series, numerical integration, etc.) can also be considered as analytical solutions.

The selected problems were picked to test the ability of the codes to model conditions important in assessing salt sites as nuclear

waste repositories. Four general processes were identified for verification:

1. Fluid transport (i.e hydrologic flow) - involves the bulk movement of water in a porous medium. Both steady-state and transient problems have been defined.
2. Uncoupled flow and trace contaminant transport - involves the transient movement of contaminants due to advection, dispersion, retardation, and decay.
3. Heat transport - involves the transient movement of heat due to convection and conduction.
4. Coupled flow with heat or solute (brine) transport - involves buoyancy flow due to density variations caused by thermal gradients or concentration gradients.

The following sections briefly describe the baseline problems selected for verification of the SWENT, CFEST, and FE3DGW and provide a few example baseline comparisons. These comparisons will be fully documented in the new code documentation reports for the VAX 11/780 versions of FE3DGW and CFEST.

The previous issue of this report (PNL-4250-3, pages 3.11-ff, 1983) provided background information on the development process involved in defining the setting for and defined the salt site-specific hydrologic flow benchmark problem. The additional specifications for benchmark problems for coupled flow and heat transport, and coupled flow and brine transport benchmark problems are briefly described below, and example results for the hydrologic benchmark problem runs are presented.

Baseline Problems-Fluid Transport

Five analytical solutions were selected from available ground-water literature for

verifying numerical 3-D ground-water flow codes; these are illustrated here by example results. These cases are as follows:

1. Flow to a well in an infinite aquifer bounded by a stream (steady state) (Thiem 1906).
2. Flow in a phreatic aquifer bounded by a partially penetrating stream (Dagan 1964).
3. Decay of a ground-water mound in a phreatic aquifer (Bear 1972).
4. Flow to a partially penetrating well in a confined aquifer (Hantush 1961).
5. Flow to a fully penetrating well in a confined aquifer (Bear 1979).

Although none of the solutions presented is fully 3-D in scope, each is designed to test various aspects of a 3-D flow code. As the very limited number and simplicity of three-dimensional analytical solutions to ground-water flow are not sufficient to test the accuracy of a model, it is necessary to choose solutions that test the performance of a code in various areas separately.

Steady-State Drawdown About a Well Near Stream

For this test case a pumping well (represented by a line sink) of infinitely small radius is located a specified distance from a fully penetrating stream of constant head. The aquifer is totally confined, homogeneous and isotropic, and unbounded on three sides. The well fully penetrates the aquifer and pumps at a steady rate. This solution tests a model's ability to predict two-dimensional flow as well as its ability to model prescribed head (stream boundary) and constant flux (upper and lower confining layers) nodes. Though this is a simple test case,

critical characteristics of a model's performance can be reviewed. Figure 3.15 illustrates the results from the FE3DGM model versus the analytical solution for a test problem of this type.

A Phreatic Aquifer Intersected by a Partially Penetrating Stream

In this test case, an approximate analytical solution proposed by Dagan (1964) for flow to drains is used to predict the height of rise of a phreatic surface in an aquifer subjected to steady accretion. The aquifer is bounded by a partially penetrating stream and a no-flow boundary below the stream and by a no-flow boundary at a specified distance from the stream. The aquifer is considered infinite in the direction parallel to the stream and infinitely deep. The aquifer is recharged at a constant rate over its areal extent, resulting in a rise of the phreatic surface. This solution is strictly 2-D and allows one to assess the ability of the code to predict a phreatic surface that results from recharge, handle converging flow patterns near the stream, and model zero flux (no-flow) boundaries.

Decay of a Ground-Water Mound in an Infinite Phreatic Aquifer

In this test case, a rectangular ground-water mound is instantaneously placed upon a homogeneous, isotropic and infinite phreatic aquifer. The initial surface of the phreatic aquifer is horizontal. The time-dependent solution to the height of the phreatic surface throughout the X-Y plane has been taken from an analogous heat-flow solution by Carslaw and Jaeger (1959). The analytical solution assumes that the initial height of

FIGURE 3.15. Comparison of the Thiem Solution with FE3DGM for a Typical Well-Stream Interaction Problem

the mound is kept small in comparison to the initial saturated thickness of the aquifer. This assumption satisfies the Dupuit approximation and neglects flow in the vertical direction, reducing the dimensionality of the problem from three to two. This solution tests the ability of the model to represent transient conditions as well as a phreatic boundary condition. This solution offers the modeler the chance to check the validity of the Dupuit assumption for various heights of mounding. At low mounding heights, good agreement is expected between the 2-D approximation and a fully 3-D numerical model.

Partially Penetrating Well in a Confined Aquifer

The analysis of Hantush (1961) solves the flow equation for the distribution of hydraulic head around a constant-discharge well that is not screened throughout the entire thickness of the aquifer. Flow to the well is considered to be radially symmetric with vertical components due to the partial penetration. The aquifer is confined, infinite in areal extent, homogeneous, and anisotropic. The solution yields time-dependent drawdowns in either piezometers or observa-

tion wells. This solution tests a code's ability to handle axisymmetric flow as well as anisotropic conductivity within the flow field. It also provides insight into a model's capability to simulate layered materials although this is not explicitly stated in the analytical solution. To model this condition, one must model the aquifer with multiple layers so as to allow the vertical flow patterns to develop. Each layer will have identical aquifer properties and initial conditions. The model's ability to achieve mass balance and continuity across these layers is essential if it is to be used in other, more complex multiple-aquifer simulations.

Fully Penetrating Well in a Confined Aquifer

The analytical solution reported by Bear (1979) solves the flow equation for the distribution of hydraulic head with time at various distances from a constant-discharge well that is screened throughout the entire thickness of the aquifer. Flow to the well is considered to be radially symmetric with no vertical flow components. The aquifer is

confined, infinite in areal extent, homogeneous, and isotropic. The solution tests the code's ability to handle time-dependent radial flow for a classic ground-water problem.

Baseline Problems-Uncoupled Flow and Trace-Contaminant Transport

Both energy and solute transport are described by the convection-dispersion equation. Several of the available analytical solutions can be couched in terms of either energy or solute mass. Thus the given solutions are used to verify both formulations.

Strict Dirichlet Boundary Condition

Coats and Smith (1964) examined the effect of employing a strict Dirichlet boundary condition as opposed to a mixed Dirichlet and Neumann boundary condition at an upstream boundary in a linear flow system. In this case the strict Dirichlet condition is used. In the following case the mixed Dirichlet and Neumann boundary condition is tested. This case is representative of situations where an upstream boundary's temperature is known, for instance, transport near a lake or river.

Mixed Dirichlet and Neumann Boundary Condition

In comparison to the previous case, this one is representative of situations where the total flux of solute mass or energy is known, for instance, transport about a well.

Point Source in Three-Dimensions with Retardation and Decay

Yeh (1981) developed a computer model (AT123D) that evaluates analytical expres-

sions for solute transport in a homogeneous isotropic aquifer. Yeh has included retardation and decay in his code. This case tests the three-dimensional capability of the codes while also testing the code's ability to simulate retardation and decay.

Effect of Dispersion on Flow Between Two Wells

Hoopes and Harleman (1967) have studied the distribution of a tracer as it flows from an injection well to a pumping well. The wells are assumed to be operating at equal but opposite flow rate. This case tests the model's ability to simulate convective dominated two-dimensional flow.

Baseline Problems - Heat Transport

Linear Heat Conduction

Carslaw and Jaeger (1959) present an analytical solution for linear heat conduction. This analytical solution is compared to the modeled results for heat conduction in the aquifer, caprock, and bedrock for representative values of thermal properties.

Energy Transport Including Caprock and Bedrock Conduction

Avdonin (1964) developed an analytical expression for linear and radial heat flow in an aquifer with an infinitely thick confining layer. This case tests the model's ability to simultaneously simulate convection and conduction in the aquifer along with conduction through the confining layers. Figure 3.16 illustrates a comparison between the CFEST code and the analytical solution for a typical test case of this type.

CFEST VS AVDONIN - GRID 29.69 M - TIME STEP 18.1 DAYS
 TIME: 1085, 2170, 3255 AND 4340 DAYS

FIGURE 3.16. Comparison of the Avdonin Solution with CFEST for a typical Overburden/Underburden Energy Transport Problem

Baseline Problems - Coupled Flow with Heat or Solute Transport

Hydrothermal Convection in Low-Permeability Media

Hodgkinson (1979) developed an analytical mathematical model for hydrothermal convection around a radioactive waste repository. Although this model decouples flow and heat transport into two linearized equations, it provides a test for fluid movement due to buoyancy in low-permeability media.

Benchmark Problems - Flow, Energy, and Solute (Brine) Transport

These benchmark problems were designed to test the ability of numerical codes to model regional hydrologic systems for layered sedimentary rocks typical of those that might be associated with bedded salt sites. In formulating these problems an attempt was made to address as many features important to

regional modeling and performance assessment as can be done in a simplified manner. These features include:

- layering
- anisotropic hydraulic conductivity (i.e., $K_h \neq K_v$)
- recharge
- discharge boundaries (rivers), outflow boundaries (held head-Dirichlet), and no flow boundaries
- interlayer communication (via borehole or fracture zone)
- water table conditions (in some layers or some areas of some layers) or totally confined conditions
- heat transport with buoyancy
- coupled solute (brine) transport).

Any eventual analysis of a bedded salt site will most likely require that the upper and lower hydrologic systems and the intervening salt strata be modeled as a single system in order that one can study the effects of potential breaching scenarios such as borehole interconnection, salt

dissolution, faulting, etc. Other pertinent considerations are that the parameter variation distributions (such as thickness and conductivity) be well defined and be representative of the kinds of changes that occur in real hydrologic systems associated with salt sites. The reader is referred to PNL-4250-3, pages 3.11ff., for the background and complete details on this development process and definition of the hydrologic flow benchmark problem and the associated data regarding basic assumptions, specifications for layering, scale, geometry, recharge, boundary conditions, discharge locations, and hydrologic parameters (hydraulic conductivity) as well as run and output specifications.

Benchmark Problem Specification for Coupled Flow and Energy Transport

This problem is designed to test the ability of coupled ground-water flow and energy transport codes to model the effect of buoyancy from repository heat loading on the regional ground-water system.

Problem Statement

This problem consists of calculating:

1. the transient effects on regional ground-water flow due to decay of radioactive wastes emplaced in the repository and
2. the transient temperature distribution induced by the repository heat loading and its interaction with the regional ground-water flow patterns.

The problem was formulated in a two-dimensional (X-Z) form based on the idealized cross-section utilized for the hydrologic benchmark problem (see Figure 3.17).

Physical Description

Figure 3.17 illustrates the cross-section to be used for this problem. The repository located in the salt section is treated as a line source for heat resulting from decay of radioactive waste. Since the interactions between regional flow and buoyant flow due to repository heat loading involve principally interactions between horizontal and vertical flow components, a cross-section representation is adequate. To test only the effects of coupled ground-water flow and energy transport, it is assumed that all aquifer waters are fresh. A uniform initial temperature distribution is assumed. All the waste is emplaced instantaneously, and the heat source resulting from the emplaced waste will decay with time.

Basic Assumptions

For this energy benchmark problem the following is assumed:

1. The system is infinite and uniform in the Y direction and is finite in the X and Z directions, with the dimensions illustrated in Figure 3.17.
2. Water in all hydrologic systems is fresh (i.e., it has zero salt content).
3. The hydrologic system before emplacement of the heat-generating waste was in steady state with the imposed hydrologic boundary conditions.
4. All X and Z boundaries have a constant temperature except the left outflow Z boundary.
5. Geothermal gradients can be neglected.
6. Water remains liquid (no steam forms).
7. Thermal expansion of rocks may be ignored (i.e., no changes in intrinsic rock permeabilities occur due to heating effects).

Problem Specifications

Geometry, layering (Figure 3.17), hydraulic conductivity, and recharge are the same as for the hydrologic flow problem. The left, top and bottom boundaries are held temperature boundaries (25°C), and the east or right boundary, along with the central river, is a convective outflow boundary for heat. Longitudinal and transverse dispersivity for all layers is 500 m and 50 m, respectively. Other energy transport parameters are shown in Table 3.5.

Initial Conditions

The initial temperature is assumed to be everywhere constant at 25°C. The regional flow system is at steady state before the repository heat source is emplaced.

Repository Heat Generation

The repository is 100 m wide and 10 m high and produces heat at a rate versus time defined as follows:

Time, yr	Heat generation rate, W/m ³
0	500E-2
100	1.91E-2
400	1.00E-2
900	4.71E-3

Output Specifications

The output of this benchmark problem is the hydraulic head and temperature distributions at t=100 and t=1000 years along with velocities at selected points within the hydrologic system.

Benchmark Problem for Coupled Flow and Solute (Brine) Transport

This benchmark problem is designed to test the ability of coupled ground-water flow and solute-transport codes to model the interaction of fluid flow and solute transport at concentrations large enough to affect the density and hydraulic properties of the hydrologic fluid (brine).

TABLE 3.5. Additional Parameters for Coupled Flow and Energy Transport

Layer Description	Specific Storage, m ⁻¹	Effective Porosity, m ³ /m ³	Rock Density, kg/m ³	Specific Heat, J/kg°K	Thermal Conductivity, W/m°K
Fluvial	1.0E-5	0.20	2000	700	2.00
Fluvial-lacustrine	1.0E-5	0.20	2000	700	2.00
Salt-shale evaporite	1.0E-5	0.20	2135	920	20.0
Limestone-shale	1.0E-5	0.05	2500	800	3.00
Limestone-shale-granite wash	1.0E-5	0.05	2500	800	3.50
Mudflat-alluvial fan delta	1.0E-5	0.20	2000	700	2.00
Transition zone	1.0E-5	0.20	2000	700	2.20

Problem Statement

This problem consists of calculating the transient effects, due to the dissolution of the bedded salt along a hypothetical dissolution front, on regional ground-water flow. The formation and development of a brine plume emanating from the dissolution zone are described. The problem is formulated in a two-dimensional (X-Z) form based on the same idealized cross-section used in the benchmark problems described above.

Physical Description

Active dissolution of the salt is assumed to occur along the 15-km front above and below the western extent of the salt layer (see Figure 3.17). Since the interactions between regional flow and solute transport along a dissolution front involve mainly interactions between horizontal and vertical flow components related to density gradients, a cross-section representation is adequate. To test only the effects of coupled ground-water flow and solute transport, it is assumed that all aquifer waters are initially fresh. A constant, uniform temperature distribution is assumed, and dissolution is assumed to begin instantaneously all along the 15-km dissolution front both on top and below the salt layer.

Basic Assumptions

For this benchmark problem the following also is assumed:

1. Darcy's law and all the other basic assumptions associated with the porous-media-continuum approach for coupled hydrologic flow and solute transport hold.

2. Temperature of all layers is the same and is constant through time.

Problem Specifications

Geometry, layering (Figure 3.17), hydraulic conductivity, and recharge are the same as for the hydrologic flow problem. The left, top and bottom boundaries allow no solute to enter or leave the system. The east, or right, boundary and the central river are convective outflow boundary locations for solute. Longitudinal and transverse dispersivity for all layers, specific storage, porosity, and rock-density-specific heat and thermal conductivity of liquid-porous media mixtures for the various parameters were discussed above for the flow and energy benchmark problem.

Initial Conditions

The initial solute concentration is assumed to be zero everywhere. The regional flow system is at steady state until salt dissolution begins.

Salt Dissolution

The salt dissolution zone consists of the 325-m left edge of the salt layer and the 15-km zone on top and below the salt layer to the left. The salt dissolution is assumed to occur at a rate proportional to the saturated concentration, C_{sat} , and the model predicted concentration along the dissolution front as follows:

$$\text{Rate} = k(C_{sat} - C)$$

The proportionality constant k is to be determined.

Output Specifications

The output of this benchmark problem is the solute concentration distributions along with velocities at points in time and space that are still to be selected. The appropriate salt-dissolution constant will be determined from a literature search and initial studies with the benchmark problem. The total simulation time will also be determined during the initial benchmark runs.

Initial Hydrologic Comparison Runs Between SWENT and FE3DGW

Early in this effort we attempted to make an initial comparison run between SWENT and FE3DGW using the same Permian Basin data set as used by INTERA during their initial modeling of the Permian Basin. ONWI supplied a copy of the modified version of SWENT used in this hydrologic study and the input data sets used to model the two hydrologic systems of importance to the Permian Basin. The two hydrologic systems important in this effort were:

1. the freshwater Ogallala-Dockum hydrologic system that overlies the Permian evaporite strata and
2. the brine system in the Wolfcamp and Pennsylvanian that lies under the Permian evaporite strata and above the lower crystalline basement rocks.

It was thought that these data sets could form the basis of the hydrologic-benchmark data set (described above) for benchmarking hydrologic codes for a salt site and that we were to investigate the use of this data set for this purpose. These early studies indicated difficulties with this approach because of discretizational differences related to

the finite-difference and finite-element approach; nevertheless, the comparisons are interesting.

The modified version of SWENT used in the INTERA hydrologic modeling effort was converted to run on the PNL VAX computer, and the two benchmark runs (Ogallala-Dockum and Pennsylvanian - Wolfcamp) were repeated on the VAX. The same grid spacing, node locations, parameter distributions, and boundary-condition distributions used with the SWENT were extracted from SWENT input and output data streams, and an equivalent finite-element representation was prepared. Figure 3.18 shows the relationship between the SWENT and FE3DGW grids for both a plan and 3-D view. As can be seen in Figure 3.18, there are difficulties:

1. In assigning parameter values such as horizontal conductivity.
2. With assigning boundary conditions because the finite-difference methodology uses only one potential to represent the potential in a given layer whereas the finite-element methodology requires two.
3. That arise when trying to assign equivalent permeabilities for the finite element when the element is located in an area of changing permeability. We tried the following methods for assignment of K_x and K_y :
 - Simple average -

$$K_x = K_y = (k_1 + k_2 + k_3 + k_4)/4$$
 - Average of the four harmonic values -

$$K_x = K_y = 0.25 * [k_{12} + k_{13} + k_{24} + k_{34}]$$
 where $k_{nm} = k_n * k_m / (k_n + k_m)$
 - Anisotropic average best method) -

$$K_x = (k_{13} + k_{24})/2$$

$$K_y = (k_{12} + k_{34})/2$$
4. In the total transmissivity related to the different discretizing methodology since

FIGURE 3.18. Plan and Three-Dimensional Views To Illustrate the Differences in Methods To Create Grids

the units' thicknesses are modeled differently with the finite-element methodology. Variations in thickness take place smoothly and not in large steps.

Results and Conclusions

Even with all the difficulties, the results of the FE3DGW comparison runs are quite similar to those of SWENT. The greatest differences show up in areas where there are abrupt changes in parameters such as conductivity and thickness. This would be expected as it is in these areas that the two codes are really modeling different hydrologic systems.

These studies have been very useful, however, since they point out an area that should be avoided in defining hydrologic benchmark problems. The hydrologic benchmark problems should have well defined hydrologic structure, permeability, and recharge- and boundary-condition distributions, independent

of any grid methodology, so that one is not simply trying to reproduce the results of the first code that ran the benchmark problem. The use of this data set from SWENT reduces the benchmark problem exercise to one of grid-matching and not one of solving a ground-water problem. Grid requirements should be dictated by the hydrologic system. Figure 3.19 compares the FE3DGW and SWENT potentiometric results for the Ogallala, where discretization differences were least important.

Initial Hydrologic Benchmark Problem Comparison Runs with the FE3DGW and CFEST Codes

The confined version of the salt-site hydrologic benchmark problem discussed above was set up, and model runs were made. Comparisons of the results between FE3DGW and CFEST indicated the same head distributions

FIGURE 3.19. Comparison Between FE3DGW and SWENT Results for the Potentiometric Surface of the Ogallala

were predicted within all layers. Figure 3.20 shows an east-west cross-section plot of model-predicted potentiometric distribution. Figure 3.21 shows an isometric view of the potentiometric surface predicted for the top surface (layer 1).

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FIGURE 3.20. East-West Cross-Section Plot of Model-Predicted Potentiometric Distributions By FE3DGW and CFEST for the Hydrologic Benchmark Problem. This cross-section plot runs along the southern boundary.

FIGURE 3.21. Isometric View of the Potentiometric Surface Predicted by the FE3DGW and CFEST Codes for the Hydrologic Benchmark Problem

Thiem, G. 1906. Hydrologic Methods, J. M. Gebhardt, Leipzig.

Yeh, G. T. 1981. AT123D: Analytical Transient One-, Two-, and Three-Dimensional Simulation of Waste Transport in the Aquifer System. ORNL-5602, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

working group is a mechanism for detailed peer review of the far-field hydrologic modeling.

Technical Progress

The first task of FY 1983^(a) was to completely document all the data sources that PNL had used in their initial modeling effort in the Assessment of Effectiveness of Geologic Isolation Systems (AEGIS). This complete data set was then used by the task force to define a basic revised conceptual model referred to as the Expanded Pasco Basin Model, to which all members could

3.2 BASALT WASTE ISOLATION PROJECT (BWIP)

3.2.1 Modeling Task Force (DB-30-10-01 - 80750)

This effort will continue the modeling activities initiated in FY 1982. The purposes of the modeling task force are to examine the Rockwell and PNL approaches to modeling the Pasco Basin, resolve differences where possible, and recommend and implement approaches for further resolution of remaining significant differences. The

(a) For background information, see PNL-4250-3, p. 3.20.

agree. The new model region extends beyond the Pasco Basin south across Horse Heaven Hills to the Columbia River and westward to the Yakima River. The first objective is to use this regional scale model to determine the boundary conditions for the Pasco Basin. Further objectives are to use the model to bound the values of horizontal and vertical hydraulic conductivity and to address the issue of whether or not the Pasco Basin is at steady state.

During FY 1983, data were interpreted and the conceptual model of the Expanded Pasco Basin region was developed. Preliminary model runs were made using the USGS/Trescott 3D finite difference ground-water flow code. The working group is currently engaged in selecting a nominal base case data set as a starting point in the planned sensitivity runs and for checking model output against field data as part of a semicalibration effort.

Also during FY 1983, a study comparing PNL and USGS data and methodologies for calculating recharge was made in response to concerns by the working group over the significance of differences between the PNL and USGS calculated recharge distributions for the Horse Heaven Hills area.

Future Activities

During FY 1984, the baseline data set will be selected and numerous sensitivity runs will be made. These runs will be designed initially to address the boundary condition issue and to determine the nature of vertical permeability within the Pasco Basin. Data on artificial recharge from man's activities (pumping, irrigation, Hanford disposal, dam construction) will be

gathered for use in making transient runs in an effort to address the issue regarding steady state.

3.2.2 Preclosure Performance Assessment (DB-20-10-01 - 80750)

The objective of this project is to develop a preliminary hazards analysis of conceptual waste package and repository designs. The preliminary hazards analysis will identify and assess the consequences of repository operational hazards and provide recommendations for improvement in safety design criteria, design concepts, or operational procedures.

Summary

An analysis of the hazards for normal repository operations has been completed, as well as an identification of preliminary accident scenarios that may impact the repository during the preclosure phase. An updated system description for the BWIP repository operations and support systems was also completed, as well as an updated review of federal criteria and regulations relevant to the preclosure safety of a repository. Available literature and the conceptual design document for the nuclear waste repository in basalt were used as background material for these efforts.

Safety Assessment of Normal Operations

An informal draft report has been completed that provides an overview of the potential safety hazards during normal repository operations. An updated version of it will be incorporated into a final project report in 1984. A Preliminary Hazards Analysis technique was used to identify the major potentially hazardous conditions of the system that could result in worker injury or

fatality. The analytical technique specifically identifies the hazardous elements, hazardous conditions and potential accidents within a system, and determines the significance of their potential effects. A separate analysis was performed for each of the following repository operations:

Mining Operations

- Site preparation and shaft sinking

- Subsurface excavation

- Drilling and preparation of placement holes

- Shaft transport

Waste Emplacement Operations

- Emplacement of remote handled waste

- Consolidation of spent fuel

- Emplacement of contact handled waste

Retrieval Operations

- Retrieval of remote handled waste

- Retrieval of contact handled waste

- Backfill and Decommissioning

Definition of Preliminary Accident

Scenarios

An informal report describing the accident sequences of potential concern for the repository in basalt has been completed in draft form. This report is being circulated for comment and will be incorporated into a final project report in 1984. The identification of preliminary accident sequences and their categorization by relative risk level will allow the design of preventive/mitigative measures into the repository system to maximize system safety. The general methodology used to identify these sequences was the fault tree logic model. Potential consequences of the accident sequences identified in this portion of the

project and recommended preventive/mitigative measures that may be useful will be prepared in FY 1984 tasks. A preliminary list of the accident types identified for the nuclear waste repository in basalt is shown below. Accidents in Category 1 include those events that are expected to occur during the construction and operation of the repository, but are not expected to have overly serious or unusual consequences. Category 2 accidents represent those that have a somewhat lower probability of occurrence during the years of repository operations, but could result in more serious consequences for the system. Category 3 accidents are those that need to be considered in the system design because of their potentially catastrophic consequences.

Category 1

- Atmospheric radionuclide release

- Exposure to unsealed hot cell

- Undetected contaminated vehicle enters prep area

- Fission gas release

- Impacts with moving vehicles

- Slips/falls

- Ventilation system

- Fire/heat

Category 2

- Atmospheric radionuclide release

- Exposure to breached casks and drums

- Impacts with moving vehicles

- Falling objects

- Caught in moving/rotating machinery

- Ventilation system

- Electrocution/shock

Category 3

- Exposure to unshielded waste canisters

- Impacts with moving vehicles

- Falling objects

3.2.3 Development of Eh-pH Sensors (DB-30-10-01 - 80752)

The objective of this work is to develop Eh and pH sensors compatible with the Dickson rocking autoclave. These sensors will provide monitoring capabilities of the oxidation-reduction environment and the hydrogen ion concentration for the hydrothermal waste-barrier-rock interaction studies. Maximum operating limits are 300°C and 300 bars pressure by the close of FY 1983.

Summary

Accomplishments during the first half of the fiscal year were 1) to redesign the Dickson autoclave to be compatible with electrochemical sensors and 2) to design Eh and pH sensors that could be inserted into the Dickson autoclave. The second half of the fiscal year was devoted to testing Eh and pH sensors.

The Eh electrode was tested to 300°C and 300 bars of pressure, meeting the original program objective. Operating limits were defined for the Eh sensor. It was discovered that the sensor must be platinum for optimum response.

An improved electrical/mechanical seal was developed for the pH electrode. Problems with reliable pH response have not been solved as yet. This program will continue in FY 1984.

Eh Sensor

The Eh sensor will measure the oxidation-reduction potential of the aqueous environment. Solubility of aqueous compounds is highly dependent upon their oxidation state.

Limits to the quantitative performance of the Eh electrode were defined. At temperatures of 200°C and above, the most oxidizing

region in which it reliably operates is in the vicinity of the hematite/magnetite equilibrium (hydrogen fugacity of about 10^{-7} atm). This region is shown in the Pourbaix diagram of Figure 3.22. Conditions more reducing than this (higher hydrogen fugacity) increase the reliability of the measurement and extend the temperature range to lower limits. Operation in environments more oxidizing to the hematite/magnetite equilibrium are of qualitative value.

Originally, platinum, gold, and titanium electrodes were evaluated in the hope that the gold and titanium Dickson vessel could be used as its own Eh electrode. We have found, however, that platinum gives such superior performance that it is the metal of choice. An Eh sensor that has been tested at 300°C, 300 bars pressure, and is suitable for use with Dickson rocking autoclave is shown in Figure 3.23.

pH Sensors

The pH is the most important variable in water chemistry. The objective of this program is the development of pH sensors suitable for use in the Dickson rocking autoclave at temperatures to 300°C and 300 bars pressure.

An improved mechanical electrical sealing system for the pH electrode is shown in Figure 3.24. Though problems remain with the zirconia-based pH electrode, the following has been learned.

- Excellent pH response is commonly found with both Coors and Zircoa yttria-stabilized zirconia pH sensors at 85°C when new.
- Temperature cycling results in significant loss of pH response and large potential drifts when retested at lower temperatures.

FIGURE 3.22. Fe-H₂O System at 200°C. Note that E_t is an absolute voltage scale which can easily be placed on the standard hydrogen electrode by examining the hydrogen line (B) at standard conditions.

- Sensors held at a constant temperature seem to remain stable over significant periods of time and can be temperature-cycled between ambient and the same elevated temperature without loss of performance at the elevated temperature.
- Grinding away the outside surface does not restore degraded pH responses, indicating that dissolution is not the cause.
- A silver internal fill reduces the impedance tenfold compared to the copper-copper oxide fill used by other researchers. Any lowering of the impedance of these extremely high-impedance sensors is desirable.

- The activation energy was measured to be 23 Kcal, a value indicating that the conduction process involves oxide ions through the ceramic.

Future work will be devoted to determining the degradation mechanism of the pH response by temperature cycling so that properly responding pH sensors can be fabricated.

3.2.4 Solubility Studies (DB-30-10-01 - 80752)

The objective of this work is to obtain radionuclide solubility kinetics and equilibria for key radionuclides in the presence of each of the geologic materials that the

FIGURE 3.23. PNL Eh Electrode for 300°C Bars

radionuclide-contaminated ground water might contact. This includes basalt, basalt flow top and secondary minerals from the Umtanum flow and the Middle Cohasset basalt. Because basalt is a dominant component of the waste package backfill, data from these experiments will complement the basalt-bentonite multicomponent solubility studies being conducted at Rockwell in FY 1983. Rock materials used in this study are supplied by the BWIP Engineered Barriers Department.

Technical Progress

Of the radionuclides investigated, only three--plutonium, radium and uranium--definitely showed that in the presence of a basalt the quantity of radionuclides added

exceeded solubility limits in a basaltic ground water only. Zirconium, lead, carbon, selenium, technetium and neptunium either persist in solution due to kinetic difficulties with precipitation or are very strongly sorbed on the basalt and therefore maintain low solution concentrations.

Reduced solubility of plutonium in the presence of Cohasset basalt is shown in Figure 3.25. C_I is the initial plutonium concentration, C is the equilibrium plutonium concentration in the solution, and (x/m) is the concentration of plutonium sorbed on the basalt. The concentration of basalt in the

TUBE YTTRIA STABILIZED ZIRCONIA
NOMINAL 1/4" OD x 8" LONG

FIGURE 3.24. PNL pH Electrode

solution did not increase as the initial concentration increased. The plutonium was either sorbed or precipitated on the basalt as fast as it was added after the solubility limit was reached. An investigation of the solids produced and filtered from solution is under way.

The uranium-silica colloid-GR-3 solution-basalt system was investigated at 82 to 25°C and 0.0001 wt% colloid in GR-3 to 1 wt% colloid, with two uranium concentrations. Figure 3.26 shows effects of temperature and the concentration of silica colloid on uranium sorption on silica colloid in the presence of basalt. Basalt sorption of

FIGURE 3.25. Equilibrium Sorption of Plutonium on Cohasset Basalt from Reducing ($0.05 \text{ M N}_2\text{H}_4$) GR-3 Ground Water at 60°C

FIGURE 3.26. Effects of Temperature and Colloid Concentration on Uranium Sorption on Silica Colloid in the Presence of Basalt for 30 Days

uranium increased with temperature, and colloid sorption decreased with decreased concentration of silica colloid and increasing temperature.

3.2.5 Hydrothermal Testing of Materials in the 325 Building Hot-Cell Test Facility (DB-30-10-01 - 80752)

The objectives of a joint PNL-WHC-BWIP hot-cell hydrothermal testing program are to provide waste-barrier-rock interactions data for quantifying the performance of waste package components in a basalt-repository environment and then evaluate and integrate these data with the BWIP package design effort. The major PNL responsibilities are to provide skills and assistance in the autoclave operation and to conduct the primary interpretation of the hydrothermal data.

Summary

In late FY 1982, a team of Hanford contractors was formed to conduct waste-barrier-rock interaction studies using fully loaded waste forms in a shielded test facility. This project is to provide data for quantifying the performance of waste package components in a basalt repository environment. The team of Hanford contractors includes Rockwell Hanford Operations (Rockwell/BWIP), PNL, and Westinghouse Hanford Company (WHC). BWIP provides program direction, WHC has built the shielded test facility and is providing analytical support, and PNL is providing skills and assistance in running the facility, is working with BWIP to design the experimental programs, and will conduct the primary interpretation of the testing data.

In addition to contributing to the shielded test facility activities, which will begin operation in early FY 1984, PNL is conducting a series of waste-barrier-rock interaction studies using waste forms doped with tracer levels of selected radionuclides.

These tests are conducted in the PNL Hydrothermal Testing Laboratory, Room 48, 325 Building. Five rocking autoclaves and ten 125-cc Ti Parr bombs in a roller oven (for 100-150°C testing) are dedicated to this effort. The tracer-testing effort allows for an expanded testing matrix due to the addition of further testing equipment. Tracer tests run parallel with the fully radioactive tests enable the effects of radiolysis to be identified. While a comparison of this parallel testing effort may not establish radiolysis-relevant reaction mechanisms, it will guide more fundamental investigations of radiolysis reactions. The tracer testing facility also allows for an investigation of the effect that other parameters have on the hydrothermal test results. By identifying key parameters using the less expensive tracer testing, we can direct fully radioactive test effort to more profitable experiments.

Technical Progress

Table 3.6 lists the details of the seven tracer tests started during FY 1983 and an eighth test planned to be started in early FY 1984. These eight tests constitute the initial series of Laboratory 48 tracer tests being conducted for the BWIP program. The first three tests are completed and the next four will continue into FY 1984. WHC is providing the analytical support for these tests. The purpose of these tests was to assess the effect that basalt and 1025 cast steel have, both alone and together, on the solubility of ^{99}Tc , ^{237}Np , and ^{239}Pu released from PNL 76-68 glass waste forms.

Figure 3.27 represents the ^{99}Tc fluid concentration data plotted against run duration for the first two tests described

TABLE 3.6. Initial Lab 48 Experimental Matrix

Experiment No.	Weight Ratio of Water:Basalt:Glass:Steel	Glass Designation
B-48-01	10:0:1:0	^{99}Tc -doped PNL 76-68
B-48-02	10:0.5:0.5:0	^{99}Tc -doped PNL 76-68
B-48-03	10:0:1:0	^{237}Np - ^{239}Pu -doped PNL 76-68
B-48-04	10:0.5:0.5:0	^{237}Np - ^{239}Pu -doped PNL 76-68
B-48-05	10:0:0.5:0.5	^{99}Tc -doped PNL 76-68
B-48-06	10:0.3:0.3:0.3	^{99}Tc -doped PNL 76-68
B-48-07	10:0:0.5:0.5	^{237}Np - ^{239}Pu -doped PNL 76-68
B-48-08	10:0.3:0.3:0.3	^{237}Np - ^{239}Pu -doped PNL 76-68

Common parameters:

1. Solution:solid ratio = 10:1.
2. Sampling schedule: First week, then every other week thereafter.
3. Run duration: 3 months.
4. Vessel condition: 200°C, 300 bars.
5. Particle sizes: Basalt: -120, + 230 mesh
Glass: -40, + 100 mesh
Steel: -18, + 60 mesh.
6. Solution analyses: pH, ICP, IC, radiochemistry.
7. Solids analyses: SEM, STEM, XRD, radchem of solids as required.

FIGURE 3.27. ^{99}Tc Concentration in Fluid Samples from Hydrothermal Tests of ^{99}Tc -Doped PNL 76-68 Glass with and Without Basalt. Run conditions were 200°C, 30 MPa, fluid was BWIP synthetic basalt ground water, and solution to solid ratio was 10.

in Table 3.6, Runs B-48-01 and B-48-02. About 50% of the total ^{99}Tc inventory is released from the glass when only crushed glass was reacted with the synthetic BWIP basalt ground water. The release of ^{99}Tc occurred quickly (in a few days) and did not increase significantly after this initial release. Because ^{99}Tc is known to line the walls of vesicles within the glass, based on autoradiography (Bradley et al. 1979), and because alkali metal pertechnetate salts are known to be extremely soluble under oxidizing conditions (Jensen 1980), high solubility for ^{99}Tc in this test was not unexpected. The glass and ground water are prepared under oxidizing conditions, and no known sink for O_2 exists in the reaction vessel for this test. We expect that the $\text{Na}(\text{?})\text{TcO}_4$ lining the vesicle walls was rapidly solubilized by the basalt water under hydrothermal conditions. Further ^{99}Tc release would require that the glass be dissolved until another vesicle was exposed to the fluid. Glass dissolves much more slowly than does the NaTcO_4 . All fluid samples obtained for both tests were split into three samples. One sample was analyzed without filtration, another was analyzed after filtration through a 4000A filter, and the last sample was analyzed after filtration through an 18A filter. The mean of the results from all three samples was then plotted on Figure 3.27. The deviation from the mean is in every case less than the size of plotting symbol for the test reacting glass with only basalt ground water. This indicates that the ^{99}Tc in the fluid is in true solution and not associated with colloids or larger particles.

Results of fluid analyses for the second test are also plotted on Figure 3.27. This test, as described in Table 3.6, is reacting equal masses of basalt and glass with basalt

ground water under hydrothermal conditions. Fluid concentration values are an order of magnitude lower than for the glass-only test during the transient period that lasts ~700 hr of run time. After this transient period, fluid concentration decreases another three orders of magnitude until the final steady-state solution concentration is reached. For the first five samples the three variously filtered fluids show no discernible filtration effect. None of the 18A filtered samples contained ^{99}Tc above the analytical detection limit, and two samples (unbracketed error bars) showed detectable ^{99}Tc for only the unfiltered sample. The three data with bracketed error bars are from the mean of the unfiltered and 4000A filtered samples. All of these fluid samples were near the analytical detection limit for ^{99}Tc , which may account for the larger errors. However, association of the ^{99}Tc with filterable material could also account for some of the apparent disagreement among the fluid analyses of variously filtered samples. The important observation is that the presence of basalt dramatically affects the solubility of ^{99}Tc by lowering it fourfold compared to glass reacted without basalt present after only 2600 hr of run time.

Although difficult to measure, we expect that differences in solution Eh may account for the differences observed in these first two tests. The glass-only test probably remained oxidizing for its duration because the glass and the synthetic water were both prepared under oxidizing conditions. The glass-plus-basalt test was also prepared under oxidizing conditions. However, fresh basalt contains considerable Fe(III) as magnetite (Fe_3O_4). As a result, O_2 can be consumed by magnetite to produce hematite, and the associated lowering of the O_2 content in the

reaction vessel will reduce the Eh. The effect of magnetite-bearing igneous rocks on the solubility of technetium has been discussed by Bondietti and Francis (1979). They have shown that the soluble species TcO_4^- was not stable in the presence of igneous rock with respect to its reduction to $\text{TcO}_2(\text{s})$. Jensen (1980) also has reported on the behavior of ^{99}Tc under reducing repository conditions and suggests that the dominant aqueous species is uncharged $\text{TcO}(\text{OH})_2$, existing also as a dimer. The total concentration of technetium is expected to be about 0.6 mg/L under these conditions if the solid phase is TcO_2 . Under yet more reducing conditions, the stable phase is metallic technetium, which has an even lower solubility. This analysis, however, does not consider the possible formation of technetium-bearing silicates, aluminosilicates, or solubility control by substitution of trace amounts of technetium in other precipitated solids.

Apparently, when basalt was present in the autoclave, the soluble TcO_4^- was reduced to $\text{TcO}_2(\text{s})$ and this insoluble phase (or whatever the solid phase was) associated itself with the finer particulates in the reaction vessel. Whether such association was due to sorption, the technetium was incorporated into a fine-grained secondary mineral, or it formed fine-grained $\text{TcO}_2(\text{s})$ is not clear from these studies. Also, the apparent change in reaction mechanism at ~1000 hr, which lowers the concentration of ^{99}Tc from an apparent transient concentration to the final lowest one, will require further study. The analysis of the solids at the end of the run is continuing. The fluid concentration for many nonradioactive species also was determined, but these data are not yet available. The solids characterization and fluid behavior for the other elements should help establish

in greater detail the mechanisms responsible for the behavior of ^{99}Tc in these tests.

These initial tests, compared to basalt-free ones, indicate that basalt lowers the solubility of ^{99}Tc . The other tests described in Table 3.6 will assess the effect basalt has on the solubility of ^{237}Np and ^{239}Pu . Other tests will measure the effect that 1025 cast steel and the combination of steel and basalt have on the solution behavior of all three radionuclides. However, certain limitations of this first series of eight tests must be recognized. No radiolysis effects were included, the ground water used was based on an ambient basalt groundwater composition instead of that expected after the water migrates through a waste package, the assemblage of waste-package components was simplistic, and the ratio of the solid-phase surface areas to fluid volume was an initial approximation of expected repository conditions only.

Future Activities

During FY 1984, and beyond, another series of tracer tests using the Laboratory 48 facility will be started. These tests will include an investigation of the effect of varying solid ratios; 1-year-duration tests; tests parallel to hot-cell tests to assess the effects of radiolysis; tests with stepwise decreases in temperature to assess the rate that the fluid composition changes to a new steady-state value; tests with methane to assess the effect methane has on fluid chemistry; tests with monoliths of solids to assess surface reactions; tests at low temperature (100-150°C) in 125-cc Ti Parr bombs using a roller oven will be compared to parallel tests in rocking autoclaves to assess whether Parr bombs, sequentially sacrificed,

will give the same fluid data as the rocking vessels at low temperatures, thus potentially expanding our experimental capability for low temperatures; tests with magnetite instead of basalt to assess the effect that the reaction of magnetite to hematite has on Eh and, if steel alters to magnetite, use this material as an "aged-canister" or accelerated test method; undoped glass plus package materials will be reacted with solutions containing excess radiotracers in order to approach solid-state solution concentration values from the saturated direction instead of the undersaturated direction. Other tests will be conducted in the tracer facility, but those mentioned above are currently planned.

The fully radioactive testing will begin in early FY 1984. Test schedules are currently being planned, but for many tests they will parallel the tracer tests to assess the effect of radiolysis. Other tests will include actual spent fuel. Unfortunately, little parallel testing can be done on tracer-level spent fuel because its complex composition makes it difficult to simulate in tracer-level formulations.

The tests described here are intended to provide data relevant to choosing a design for a waste package in a basalt repository. The aim is to understand the effects that various parameters and waste-package components have on the solubility of key radionuclides under repository-simulated conditions and to obtain data usable to the various BWIP modeling efforts for predicting the long-term behavior and radionuclide release rates from a waste package located in a basalt repository. The experimental program is designed for flexibility to accommodate the needs of the BWIP as it evolves and to

adjust experimental directions as the nature of waste-package components and rock interactions, under hydrothermal conditions, are better understood.

References

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3.2.6 Structural Barrier Materials (DB-30-10-01 - 80752)

The Structural Barrier Materials Task has as its objective the characterization and recommendation of metallic materials for use as structural barrier components in high-level nuclear waste packages for a Hanford basalt repository medium.

Summary

Two major material degradation modes were addressed: general (uniform) corrosion and stress-corrosion cracking. The general corrosion was determined in autoclave studies with and without the imposition of gamma irradiation. Resistance to stress-corrosion cracking was determined by hydrothermal slow-strain-rate studies. Primary emphasis was placed on cast and wrought ferrous materials, as the data obtained to date have indicated that these materials are satisfactory in low-ion-strength basaltic ground waters.

General Corrosion

In the general corrosion study, specimens of ductile (nodular) cast iron, 2-1/2% Cr - 1% Mo cast steel, 1-1/4% Cr - 1/2% Mo cast steel, 1025 cast steel, and 1020 wrought steel were exposed to flowing simulated Grande Ronde basalt ground water in refreshed autoclave systems at 250 and 150°C. Synthetic ground water was pumped through the autoclaves on a once-through basis from a storage reservoir sparged with an Ar-20% O₂ gas mixture at a flow rate of ~35 mL/hr. The water, termed "oxic" because of its 6 to 8 ppm O₂ content, flowed upward through a bed of crushed basalt rock 3 to 5 cm deep before contacting the specimens.

The general corrosion of the candidate mild and low-alloy steels and a ductile cast iron is not overly severe. At 250°C, the general corrosion rate is <0.30 mil/yr (7.6 µm/yr) after 17 months exposure, except for two specimens of the 1-1/4% Cr - 1/2% Mo alloy, which showed unusual nonuniform attack. At 150°C, the general corrosion rate is <0.50 mil/yr (13 µm/yr), except for several specimens of 1020 wrought steel, which showed unusual localized corrosion. Susceptibility of the candidate alloys to pitting attack is of much greater concern at present than are the modest penetration rates associated with general corrosion.

Irradiation-Corrosion

The irradiation-corrosion tests are performed similarly to the general corrosion tests, except that the test autoclave is exposed to ⁶⁰Co gamma irradiation at a dose rate, to the contained ground water, of ~3 x 10⁵ rad/hr. After 13 months exposure at 250°C, the highest rate observed was

0.43 mil/yr (11 µm/yr). This corresponds to a corrosion rate enhancement of 2-3 compared with unirradiated test data.

Slow-Strain Rate Tests

Slow-strain-rate (SSR) testing is used to determine the relative susceptibility of different canister materials to stress-corrosion cracking (SCC). SSR tests were performed using a refreshed autoclave system containing a layer of crushed basalt, as in the general- and irradiation-corrosion tests. Tests were also done in an air environment, considered inert to the ferritic specimens. A wrought AISI 1020 steel was emphasized in the tests. The ductility of the steel was diminished when tests were done at a strain rate of 2 x 10⁻⁷/sec and a temperature of 150°C, relative to tests done at higher strain rates in ground water or tests done in air. The ductility of the material was not affected by strain rate when tests were done in air, or by ground water relative to air when tests were done at a strain rate of 10⁻⁴/sec. Fracture surfaces of specimens showing low ductility had features indicative of environmentally enhanced cracking, including intergranular fracture, transgranular cleavage, and secondary cracking.

3.2.7 Sorption Studies (DB-30-10-01 - 08753)

The objective of this work is to obtain radionuclide sorption-desorption kinetics and equilibria for key radionuclides in the presence of each of the geologic materials that the radionuclide-contaminated ground water might contact. This includes basalt, basalt flow top and secondary minerals from the Umtanum flow and the Middle Cohasset basalt. Because basalt is a dominant component of the waste package backfill, data from these experiments will complement the basalt-bentonite multicomponent solubility studies being conducted at Rockwell in

FY 1983. Rock materials used in this study are supplied by the BWIP Engineered Barriers Department.

Technical Progress

Sorption kinetic studies were completed on Umtanum and Cohasset basalt for zirconium, plutonium, and radium. At least three initial radionuclide concentrations were used under oxidizing and reducing conditions at 60°C in GR-3 synthetic ground water. Zirconium and radium were readily sorbed under both reducing and oxidizing conditions, while plutonium was most efficiently sorbed under reducing conditions. Figure 3.28 shows plutonium sorption kinetics for three plutonium concentrations onto 16-to-60-mesh Cohasset basalt.

A uranium and two radium flow-through basalt columns were continuously loaded for the past 7 months. The radium columns, after 6000 to 7000 pore volumes, attained only

about 12% loading. The uranium column was fully loaded as shown in Figure 3.29. A very slow flow rate was required to avoid high leakage rates with the uranium column.

Kinetic technetium and selenium sorption experiments were conducted at 150°C and 1000 psig argon on a backfill mixture of Umtanum basalt and standard bentonite. Figure 3.30 shows a portion of the technetium kinetic data for two technetium concentrations. The Tc(VII) of the initial radionuclide was eventually all reduced to the less soluble Tc(IV).

3.2.8 Repository Seal Design Engineering (DB-30-10-02 - 80751)

The FY 1983 objectives of this program are to 1) identify and evaluate the state-of-the-technology related to the degradation of proposed repository sealant materials and 2) develop a preliminary strategy for a statistically valid testing plan and will ensure the adequacy of repository seals.

FIGURE 3.28. Plutonium Sorption Kinetics on 16-to-60-Mesh Cohasset Basalt from Reducing (0.05 M N₂H₄) GR-3 Ground Water at 60°C

FIGURE 3.29. Sorption of Uranium by a 16-to-60-Mesh Cohasset Basalt Column from Oxidizing GR-3 Ground Water at 60°C in Response to Flow Rate. $C_0 = 8.680 \times 10^{-7}$ M U.

FIGURE 3.30. Kinetic Sorption of Technetium on Umtanum Basalt-Untreated Standard Bentonite (3:1 wt ratio) in GR-3 Ground Water Deoxygenated by Argon Purging Before Heating the System to 150°C at 1000 psig Ar

Technical Progress

The approach to achieve the objectives involved 1) an evaluation of a similar regulatory process (the licensing of drugs and food additives) involving the extrapolation of limited-time data to determine if techniques and methods used could be transferred to repository licensing; 2) an evaluation of the ancient construction materials to determine if suitable degradation data could be identified that would permit better extrapolation of current or future generated degradation data; 3) an evaluation of the available literature concerning the degradation of cementitious materials and clay-basalt mixtures that are currently being considered as sealant materials in the expected BWIP repository environment; 4) an evaluation of methods of extrapolating limited-time data as it might pertain to the degradation data; and 5) using the information, or lack thereof, from the four evaluation steps, develop a preliminary strategy for a statistically valid testing plan for degradation testing of cementitious materials and clay-basalt mixtures.

Major findings of this study included:

1. Continued testing after repository licensing to verify seal behavior predictions is desirable.
2. The significant chemical reaction occurring in ancient lime-based cementitious materials is carbonation, which is unlikely to occur to a significant extent in the shaft seal during its lifetime if currently reported hydraulic conductivity values for basalt are correct.
3. Degradation data pertinent to the shaft-seal environment for cementitious materials and clay-basalt mixtures that might be used for shaft seals are nearly nonexistent. Therefore, an extensive testing program to determine the changes in properties as a function of time, i.e., degradation, is warranted.
4. No unique method of extrapolating limited-time test data was identified that will implicitly define defensible degradation predictions. The best way to increase prediction reliability is to decrease uncertainty in the data base by obtaining a sufficient number of testing data points.
5. Accelerated testing is required to obtain adequate data for seal-behavior modeling predictions.
6. Chemical reactions, either naturally occurring or with the ground water, will be the primary driving force for changes in sealant material properties.
7. Temperature and a significant increase in surface area are the primary accelerating parameters for determining the chemical changes that will occur in sealant materials and should be used to determine reaction products.
8. Temperature is the primary accelerating parameter for determining changes in properties of the sealant materials and should be used to obtain the needed data on both the original starting materials and simulated intermediate metastable phases (as determined from the reaction product tests).
9. It is important to study the degradation properties of the sealant material in both the wet and dry conditions.
10. At least four, and possibly five, specimen geometries will need to be tested to determine the changes in properties of the sealant materials; only two geometries, solid and powder, are required for testing to determine reaction products.

3.3 NEVADA NUCLEAR WASTE STORAGE INVESTIGATIONS (NNWSI) (DB-30-20-01 - 1690/1)

3.3.1 Waste Package

The primary objective of this research is to understand elemental release from the waste form, both with and without the presence of a metal, in a tuff repository environment.

Summary

In an effort to understand release from a waste package system in a tuff repository, a series of interactive experiments was conducted in tuff ground water using 76-68 glass, tuff rock, and ferrous metals. The 76-68 glass was chosen because of the large existing data base and because it represents, in a generic sense, a commercial waste glass. The metals used were both 304L and 316 stainless steels as well as 1020M mild steel, candidate metals for incorporation into a tuff repository. The findings were that tuff dominates the waste package system if enough rock surface area is present, that is, about 100 times more than glass. Rock-dominated systems result in very little glass reaction and release due to high silica concentrations in solution. The presence of 300-series stainless steels has no effect on waste-form or waste-package behavior. The presence, however, of even a small quantity of the more reactive 1020M mild steel results in a system dominated by metal. This causes more glass reaction due to the formation of iron-silicate compounds, but the iron sorbs uranium from solution, resulting in less uranium available for transport.

Technical Progress

The purpose of this report is to summarize current progress. All reported results were obtained by static leach testing following a procedure similar to MCC-1. Data are reported as Tests 1, 2, or 3. These tests are described as follows:

- Test 1. 76-68 glass in tuff ground water (Well J-13) at a sample surface-area-to-solution-volume ratio (SA/V) of 10 m^{-1} .
- Test 2. 76-68 glass + tuff rock + tuff ground water with an $\text{SA/V} = 10 \text{ m}^{-1}$ and with monolithic rock. The rock geometric surface area equals that of the glass. The actual rock surface area (N_2 BET) equals $\sim 0.25 \text{ m}^2$, which compares to $\sim 2 \times 10^{-4} \text{ m}^2$ for the glass sample. Thus the system should be rock dominated.
- Test 3. 76-68 glass + tuff rock + 304L SS. The test is identical to Test 2 except for the addition of a piece of monolithic metal of equal surface area to the glass sample.

This represents only part of the test matrix. Variations in SA/V ratios and in constituent surface area ratios are included in the complete matrix given in Table 3.7.

Data Summary

The current data can be summarized as follows:

- In the absence of 1020M mild steel, tuff rock powder dominates the system.
- Tuff rock monolithic samples do not have a large effect on 76-68 glass release characteristics even though the rock monolith has a large N_2 -BET surface area.
- Increasing amounts of rock powder do not detectably decrease B release (it is

TABLE 3.7. Test Matrix

Test	Temp., °C	Time, Days	Waste Form Morphology	Metal ⁺⁺⁺	SA/V ⁺	Rock ⁺ Morphology
TEST 1						
I-40	40	3- 182	MONO		10	N.A.
I-70	70	"	"		"	"
I-90	90	"	"		"	"
I-150	150	3- 91	"		"	"
TEST 2						
II-40	40	3- 91	MONO		10	MONO
II-70	70	3-182	"		"	"
II-90A	90	"	"		"	"
II-90B	90	"	"		"	0.1 g ROCK POWDER
II-90C	90	"	POWDER -40+80		100	1 g ROCK POWDER
II-90D**	90	"	"		100	0.1 g ROCK POWDER
II-90E	90	"	POWDER -100+200		400	4 g ROCK POWDER
II-150	150	3- 91	MONO		10	MONO
TEST 3						
III-40	40	3 -182	MONO	304 L	10	MONO
III-70	70	"	"	"	"	"
III-90A	90	3 - 91	"	"	"	"
III-90B**	90	"	POWDER -40+80	++	100	0.1 g ROCK POWDER
III-90C	90	"	MONO	1020 M	10	MONO
III-90D	90	"	"	316 SS	"	"
III-90E	90	3 - 28	POWDER -40+80	1020 M	100	0.1 g ROCK POWDER
III-150	150	3 - 91	"	304 L	"	"
TEST 4						
IV-90A	90	3 - 182	NONE	NONE	N.A.	MONO
IV-90B	90	"	"	"	"	0.1 g ROCK POWDER
IV-CM	40	1	"	"	"	MONO
IV-CM	70	"	"	"	"	"
IV-CM	90	"	"	"	"	"
IV-CM	150	"	"	"	"	"
IV-CP	40	1	NONE	NONE	"	0.1 g ROCK POWDER
IV-CP	70	"	"	"	"	"
IV-CP	90	"	"	"	"	"
IV-CP	150	"	"	"	"	"
IV-90D	90	3 - 91	"	"	"	MONO
(Tuff monolith preleached for 1 day at 90°C)						
IV-90E	90	3 - 91	"	"	"	0.1 g ROCK POWDER
(a) Prewashed in sonic cleaner (in tuff water). (b) preleached for 1 day at 90°C (in tuff water).						
IV-23-PO	23	-	"	"	"	0.1 g ROCK POWDER
(a) Prewashed in sonic cleaner for 5 minutes. (b) Solution filtered 0.45 µm.						
IV-MO	23	-	"	"	"	MONO
(a) Sonic cleaned for 5 minutes.						
IV-90F	90	3 - 91	MONO	"	10	MONO
(a) Tuff rock monoliths preleached for 1 day at 90°C in tuff water.						
IV-90G	90	3 - 91	MONO	"	10	0.1 g ROCK POWDER
(a) Tuff rock powder sonic-cleaned. (b) Tuff rock powder preleached for 1 day at 90°C in tuff water.						
IV-90	90	3 - 91	NONE	NONE	N.A.	NONE
(a) Tuff water only.						

* Glass sample surface area/leachate volume.

** Duplicate experiments made.

+ Rock monoliths had the same geometric surface area as the glass sample.

Rock powder was -60 mesh.

++ Metallic surface area is ten times glass monolith surface area to be consistent with higher SA/V.

+++Metallic surface area was equal to glass surface area.

already very low) but have a significant effect on reducing uranium solution concentrations.

- When 1020M mild steel is present, it appears to dominate the system, significantly increasing glass reaction. However, the 1020M steel also scavenges uranium from solution, probably as a result of iron hydroxide formation, increased pH, and reduced Eh.

3.3.2 Structural Barriers

The objective of the Structural Barriers Program is the characterization of metals considered potentially useful as structural barrier materials in high-level nuclear waste packages intended for a Nevada tuff repository.

Summary

Two major metal degradation modes were addressed: general (uniform) corrosion and stress-corrosion-cracking. General corrosion rates were determined in autoclave studies with and without the imposition of a high-intensity gamma radiation field. Resistance to stress-corrosion cracking was determined by hydrothermal slow-strain-rate studies. Primary emphasis was placed on 1025 wrought steel, wrought 9% Cr - 1% Mo steel, and 304L stainless steel.

General Corrosion

The general corrosion study involved corrosion testing of specimens of 1025 wrought steel, wrought 9% Cr - 1% Mo steel, and AISI 304L steel, in both the solution-annealed condition (1050°C) and the solution-annealed condition with sensitizing heat treatment (600°C for 10 hr). The specimens were

placed in an autoclave half full of crushed Topopah Springs tuff rock. J-13 well water obtained from the Nevada Test Site, sparged with air at ambient temperature, was pumped through the autoclave, from bottom to top, at a flow rate of ~35 mL/hr. The autoclave was held at a temperature of 150°C.

At the end of each exposure period selected specimens were stripped of their surface deposits in formaldehyde-inhibited HCl and weighed. The weight change was converted into a metal penetration rate. After film stripping, the samples were also inspected for signs of nonuniform attack, e.g., pitting.

The maximum exposure duration obtained in this test was 5 months. After this time, the maximum corrosion rates observed were 1.9 mil/yr for the 1025 wrought steel and 0.39 mil/yr for the 9% Cr - 1% Mo steel. The highest rates for these materials were found in the water-plus-rock region of the autoclave. The 304L stainless steel corroded at a very low rate, <0.008 mil/yr, regardless of autoclave position or heat treatment.

All the 9% Cr - 1% Mo steel samples showed some degree of pitting attack. This mode of attack was accentuated in the water-plus-rock region of the autoclave. The 1025 wrought steel specimens underwent some nonuniform attack, apparently of an intergranular nature, in all cases, and some crevice-corrosion attack occurred in the water-plus-rock region of the autoclave. All 304L stainless steel specimens appeared to be in excellent condition.

Irradiation Corrosion

Specimens of 9% Cr - 1% Mo wrought steel, 1025 wrought steel, and AISI 304L stainless

steel were exposed to tuff water and rock, as in the general corrosion studies, but at two different test temperatures, 105 and 150°C, and with superimposed ^{60}Co gamma irradiation, 3×10^5 rad/hr and 6×10^5 rad/hr, respectively. After a 3-month test period, all materials showed a several-fold corrosion rate enhancement due to the radiation field, although the short-term nature of the data and its inherent scatter preclude a quantitative assessment of the effect. The water-plus-rock region appeared more corrosive to the 9% Cr - 1% Mo alloy in the irradiation-corrosion test, as in the unirradiated test.

X-ray diffraction analysis of the surface layers on 1025 and 9% Cr - 1% Mo specimens from both the irradiated and nonirradiated tests typically reveal the presence of clay-type mineral of layered structure, with occasional evidence of Fe_3O_4 .

Slow-Strain-Rate-Tests

Slow-strain rate testing has been performed primarily on AISI 304L stainless steel, in the solution-annealed condition and in the post-sensitizing-heat treatment condition, to determine if there is any observable susceptibility to stress-corrosion cracking (SCC) of this material in a J-13 well-water environment at 150°C. Tests performed at strain rates of 1×10^{-4} /sec and 2×10^{-7} /sec have not revealed any susceptibility to SCC, regardless of environment or material heat treatment.

3.4 OFFICE OF NUCLEAR WASTE TERMINAL STORAGE INTEGRATION (ONI)

3.4.1 Simplified System Performance (AP-05-15-15 - 80742)

The four tasks of this program are each directed at improving the capability of HQ to 1) manage the performance assessment activities of the NWTs projects and 2) make performance assessment-based policy decisions.

Summary

Of the program's four tasks, three were active in this reporting period. The fourth had been completed the first half of the fiscal year. The first task is to develop and document a simplified far-field performance assessment simulator. Such a simulator (SCOPE) was developed this fiscal year and documentation was completed. A modified version of SCOPE also was developed that is capable of addressing incongruent releases.

The second task involved examining the INTRACOIN results and resolving their differences. It was found that contrary to speculation of the INTRACOIN participants, the differences arose principally from differing interpretations of the problems.

The major effort of the third task involved an examination of selected aspects of NRC performance assessment methods and a comparison of these with NWTs project methods. It was found that the codes used by the NRC and DOE were similar and should be

expected to give the same results. However, the NRC is apparently adopting a risk-based approach to uncertainty. The NRC's approach to uncertainty was found to be based on Monte Carlo Latin-Hypercube techniques. PNL recommended that certain improvements in this technology be developed.

Simplified Simulator

A simplified simulator for repository performance assessment was developed and documented. This simulator, the Simplified COdes for Performance Evaluation (SCOPE) system, is a series of integrated computer models designed to help provide understanding of possible behavior patterns of radionuclides from radioactive waste.

The computer programs that make up the SCOPE system (Version 1.0) can be separated into three groups (see Figure 3.31). The first, the BAIRN system, comprises four programs that simulate ground-water transport of radionuclides from the repository through a ground-water system to the biosphere. Program EXPOSE represents the second group; it uses the results of BAIRN to calculate the integrated exposure to radionuclides in accordance with regulations set up by the Radiation Protection Programs (1982). The third group consists of dose codes PABLM and ALLDOS. These dose codes use the results generated by BAIRN to provide a detailed estimate of potential radiation doses to man (Streng et al. 1980; Napier, Kennedy and Soldat 1980). The SCOPE system also includes two CONVERT programs, CONPABLM and CONALDOS, which translate the information from the BAIRN system into a form that can be understood by the dose codes.

More specifically, BAIRN uses analytical solutions to the equation for one-dimen-

sional solute transport for up to a three-member decay chain [developed by Pigford's group at the University of California at Berkeley (UCB)]. Analytical solutions for single radionuclides are performed by BAIRN1; two- and three-member decay chains are simulated by BAIRN2 and BAIRN3, respectively. The equation may be written:

$$B_i \frac{\delta C_i}{\delta t} = D \frac{\delta^2 C_i}{\delta x^2} - V \frac{\delta C_i}{\delta x} - B_i \lambda_i C_i + B_{i-1} \lambda_{i-1} C_{i-1}$$

where C is concentration, B is the retardation factor, D is the dispersion coefficient, V is the pore velocity, and λ is the radioactive decay constant. The subscripts refer to the position of the radionuclide in the decay chain. Principal simplifying assumptions for BAIRN's analytical solutions are as follows:

- Sorption is in equilibrium.
- All elements have infinite solubility.
- Dispersion is the same for all nuclides.
- Fluid flow is steady state.
- Radioactivity is released into ground water through a band release.
- A uniform one-dimensional flow path is used.

BAIRN4 approximates chains of four or more radionuclides by combining the results of one-, two-, and three-member chain solutions of the equation. The results of BAIRN4 are written out in a file that is compatible with the exposure and dose codes.

Program EXPOSE uses a given set of criteria to estimate the potential hazard to man from the transport of radionuclides to the biosphere. EXPOSE uses the results of BAIRN1 through BAIRN3 to sum the curie load

FIGURE 3.31. Generalized SCOPE System

passing through the boundary of an aquifer over time. These results are compared to the given criteria. The criteria normally used are those developed by EPA for determining compliance with its standards.

Programs ALLDOS and PABLM calculate internal radiation doses to man from radionuclides in food products and external radiation doses from radionuclides in the environment. Both programs use the results of BAIRN as well as input from the user for these calculations. The results from ALLDOS and PABLM are similar; they differ mostly in operational details.

During this reporting period, development and documentation of the initial version of SCOPE system was completed. A modified version of the SCOPE system also was developed, in which incongruent leach rates are permissible. It thus permits situations to be considered in which solubility controls the release to the far-field.

INTRACON Reconciliations

INTRACON participants were invited to apply their far-field transport methods to a

series of hypothetical situations involving coupled migration of transuranics. These scenarios were considered sufficiently well-defined to represent a test of capability for each participant's approach.

Two approaches taken by participants, UCB and PNL, are generally regarded as representative of solutions to the one-dimensional contaminant transport problems. The UCB approach analytically solves the convective-dispersive partial differential equation on either an infinite or semi-infinite domain for each nuclide species; releases to the environment are defined as those concentrations passing an observation point within the domain; and the analytical solutions are evaluated using computer codes. The PNL approach [multicomponent mass transport (MMT)] uses a discrete-parcel random-walk computer code to implement a heuristic physical model on a finite domain. The MMT method does not (demonstrably) produce the solution to the same coupled partial differential equations. Releases are determined by nuclide quantities exiting the domain. These two approaches gave small differences in results for most INTRACON problems.

Those differences, although small, were significant because they were not expected nor understood. Participants ascribed them to the differing domains and methods of defining environmental release for the two approaches. The research reported here was undertaken to determine the reasons for the differences between the PNL and UCB results.

To assess the effects of differences in transport domain and release boundary condition, a code developed by van Genuchten was extended to include a stochastic dispersion description. This code, SICHAIR, incorporates dispersion by using an ensemble of analytical solutions on a finite interval. By making the interval very large (compared with the distance between source and observation point) the infinite or semi-finite domain results could be approximated. Thus SICHAIR can produce a solution on a semi-infinite, infinite, and finite domain. This allowed explicit consideration of the effects of domain size and boundary conditions.

Conclusions

The UCB and MMT models had distinct conceptualizations. The concentration boundary conditions formulated in MMT were found to have a fundamentally different conceptualization than that used by UCB. The observation by INTRACOIN participants that discrepancies could be entirely attributed to the outlet boundary condition and the extent of domain was based on their belief that identical inlet conditions were simulated. This was not found to be true. An apparently good comparison for inlet concentration-type boundary condition cases was found to be fortuitous. Discrepancies in results for source-type conditions, however, reflected the conceptual differences in the outlet conditions.

It was found that within their respective formulations both models yield correct results. Differences are usually due to interpretation and implementation of boundary conditions. Generally we found that MMT compared well with analytical solutions based on pairs of inlet and outlet conditions when appropriately interpreted. However, exactly equivalent analytical solutions for nuclide chain transport in a finite domain are not available for comparison.

This study also indicated that the formulation of MMT was not best suited for comparison in terms of outlet nuclide concentration. The MMT model was actually designed to predict outlet flux breakthrough, whereas the analytical solutions of UCB are for concentrations. An assumed convected outflow condition is employed by MMT to estimate outlet concentration. However, it is not certain that the condition actually may hold for MMT. It appears that a zero-gradient condition holds for flux instead.

Significance of the Study

The significance of this study resides in a demonstration that field-scale transport has an alternate and more appropriate stochastic-convective representation. More than merely resolving the question of boundary-condition influences on INTRACOIN simulation results, this study addresses the issue of proper representation of field-scale dispersion. Determination of appropriate boundary conditions will be absolutely essential for making fully three-dimensional predictions of contaminant migration. The impact of various diffusion-related boundary conditions for simple one-dimensional systems must therefore be completely understood by modelers before proceeding to more complicated field-scale simulation problems.

This study suggests that the considerable influence of particular boundary conditions is a theoretical artifact of a Fickian diffusion description, when applied to field-scale conditions. The related issue is not avoided by proclaiming that local diffusion is a negligible process. Field-scale dispersion is a substantial effect usually requiring representation by much greater "effective" diffusion coefficients. The stochastic-convective method demonstrated here resolves the issue by emphasizing how dispersion results from flow-velocity variability instead of from an inappropriate diffusion process. The inordinate effect of boundary conditions is shown to be suppressed by placing controlling emphasis on flow-velocity statistical variation. That stochastic variation includes both the effects of interior system variation and boundary conditions. Thus more relevant transport parameters are identified by developing a model based on a more appropriate conceptualization.

Technical Assistance

The principal effort conducted under this task was a review of aspects of the NRC's performance assessment methods and comparison of these methods with DOE Project methods.

The areas of performance assessment focused on in this effort were those of far-field models for assessing geohydrologic flow and transport and environmental consequences. The actual bibliography of material reviewed was found to be a somewhat limited subset of the total bibliography of material which could have been reviewed. Inspection of the additional unreviewed material by title and attendance at NRC review meetings on perform-

ance assessment indicates that little new information on NRC performance assessment method was missed.

The focus of the review was to determine if there are any potential inadequacies in either DOE or NRC approaches to geologic isolation system performance assessment or if there are potentially important differences in performance assessment methods that would lead to problems in licensing or that would require DOE to obtain additional site characterization data not required by their methods.

The comparative evaluation of the proposed NRC and NWTS codes for use in far-field geohydrologic performance assessment indicates that while the actual codes may have different names and development histories, they solve the same equations and, when properly applied to the same data sets, can be expected to give the same results. The NRC program for documentation, verification and benchmarking of performance assessment codes, which all NWTS contractors are adhering to, is adequate to ensure to DOE and NRC that the codes are adequate and error-free within reasonable limits. It is noted that all the codes proposed for use by both NRC and NWTS contractors are of the deterministic type.

General data requirements for both DOE and NRC performance assessment models are likely to be much the same. Any differences in data needs are expected to arise from different approaches being chosen for sensitivity and uncertainty studies and different conceptual models being proposed to describe geohydrologic system behavior. As long as DOE site characterization contractors realize that some form of uncertainty and sensitivity analysis is going to be required and "reasonable" conceptual models of the site are not prematurely excluded, no problems should

arise relative to lack of necessary site characterization data. It became evident that NWTs contractors must avoid locking-in on a single conceptual model of a complex site too early. To do so can mean that potentially useful site characterization data will not be obtained that may eventually be required to explain system response. The NRC's present position of accepting only "traditional" data analysis and interpretation techniques was questioned because it could preclude the use of new technology.

It was found that DOE needs to concern itself more with the important issues of who interprets the data and applies the codes and how they are applied. DOE needs to ensure that they are answered by requiring appropriate qualified peer review of the approaches to modeling and performance assessment in the early as well as the later stages of the project. PNL recommended that all modeling and performance assessment work, at least in geohydrology, be peer-reviewed by independent, recognized authorities in the field at various stages throughout the project.

Two major differences between the NRC and DOE approaches to performance assessment were identified. These lie in the area of risk assessment and the approach to sensitivity and uncertainty analyses. The NRC is indicating that a full risk assessment approach will be required similar to the WASH-1400 reactor safety analysis in order for DOE to demonstrate compliance with the EPA Table 2 release rates.

The NRC's approach to handling uncertainty (Monte Carlo technique) could potentially cause difficulties in licensing a site. This currently supported uncertainty method does

not appear to be well suited for systems for which parameters are correlated. It also contains no constraints for limiting parameter distributions to that subset which produces "realizations" of potential distributions within the realm of observations. It was noted that uncertainty in boundary conditions, recharge, conceptual models, and stratigraphy are not being addressed systematically by either DOE or NRC. DOE, namely the ONWI program, is following an integrated approach to sensitivity and uncertainty by relying upon the "adjoint" approach and first-order perturbation techniques. These are augmented by correlated Monte Carlo sampling to benchmark variance estimates. PNL recommended that DOE work jointly with NRC to determine a consistent approach for quantifying uncertainty in ground-water systems so as to include only realistic realizations.

The last area of potential concern in the geohydrologic performance assessment area is the rapidly growing awareness in the scientific community of the deficiency of the traditional "convective-dispersive transport equation" to correctly describe transport in a geohydrologic system. PNL recommended that DOE maintain an awareness of work being performed in this field and the changing attitude toward the applicability of this traditional equation to geosphere transport so as not to be caught unaware by new requirements.

3.4.2 RECON Repository Cost Analyses

The objective of this program is to develop a verified repository economics model and data base to evaluate the cost impacts of preliminary repository design trade-offs and to estimate overall waste disposal costs.

Documentation and User's Manual

During the second half of FY 1983 the final milestone of this program was completed with the publication of the Documentation and User's Manual. It was issued in May as PNL-4465, RECON: A Computer Program for Analyzing Repository Economics. It includes improvements made to the model as part of another DOE program that allow modeling of the borehole in the wall emplacement and also co-emplacement of low-heat-generating wastes with HLW.

Description of Model

The model is a computer program designed to estimate costs of mined geologic repositories based on parametric data input. Using it, preliminary cost estimates of the impact of design changes can be made. Although it generates estimates less precise and detailed than those by an architect engineer, it can generate first-order estimates much more quickly and cheaply and thus can be used to focus on areas where more detailed design efforts are cost-effective and necessary.

It is emphasized that the model is undergoing further modification, improvement, and verification. Attempts to use RECON without a thorough understanding of repository design limitations could lead to erroneous results and conclusions. The authors thus recommend that they be consulted first by anyone desiring to employ it.

Basic model input parameters describe facilities, construction times, shafts, mine design, emplacement limitations, waste flows available for disposal, waste processing parameters (labor, materials, utility, and equipment requirements), facility construction costs and unit labor, materials, utility

and equipment costs. Using this information, the model determines the facility requirements for receiving, packaging, transporting, and emplacing the wastes. Based on the facility requirements, it calculates labor, material, and equipment requirements. Labor requirements are calculated in shifts based on available working days. From the shifts and days worked, utility requirements are calculated. Requirements to replace equipment are calculated based on equipment life (stated in years or units processed) and processing rates. All of these requirements are calculated year by year for each waste type, thereby simulating actual repository operations.

Excavation of the mine is modeled assuming initial shaft, shaft pillar, and main corridor excavations followed by room excavations needed to emplace waste volumes received the following year. Hoisting, surface storage, and offsite disposal tonnages are also calculated. The user has the option of allowing the model to calculate requirements and costs for mining labor materials and equipment for the above operations or of inputting unit costs for the above rock operations. Mine excavation requirements are based on input data describing room, panel and corridor dimensions and spacings. Density of waste emplacement in rooms is calculated by the model based on minimum waste spacing (determined by very-near-field thermal criteria or by rock strengths), waste-package thermal densities, and far-field and near-field limiting thermal densities. Annual excavation requirements are then calculated for each waste type using the emplacement density, annual waste units requiring disposal, and room and corridor dimensions.

Backfilling operations are modeled using input data that determine startup of these

operations and annual backfilling rates. The model alternatively uses the annual rock hoisting (lowering) capacity as a default rate if no backfilling rate is specified (obviously a specified rate should be less than the default rate). Based on excavated volumes, the model determines the annual rock mass backfilled and the duration of backfilling operations if these extend beyond waste emplacement operations. Cost calculation methodology is specified by the same option governing the other rock logistics calculations.

Startup of decommissioning and sealing operations is dynamically determined by either the end of waste operations or the end of backfilling operations. Waste operations cease either at the end of an input time period or when the total underground area requirement exceeds a maximum size. Backfilling operations end when all excavated rooms are backfilled. During decommissioning operations, the remaining corridors and shaft pillar areas are backfilled, the shafts are sealed and the surface facilities are decommissioned. Backfilling costs are determined as previously explained. The model uses unit sealing costs together with shaft diameters to calculate total sealing costs. Decommissioning costs are calculated based on an input percentage of total surface facility costs.

Also included in the costs are land, licensing, site preparation, and startup costs. Land, licensing, and site preparation costs are input determined, while startup costs are based on an input percentage of total construction costs.

Contingencies account for unidentifiable costs of labor, materials, and equipment and other unspecified items. These are calculated by multiplying input percentages by

construction costs, waste operations costs, rock operations costs, and decommissioning costs.

Output tables show summaries of total construction, waste operations, rock operations, and decommissioning costs by waste type. Further breakdowns of costs within these categories are shown in backup tables as a function of time. Levelized unit costs are calculated per unit mass, unit volume, and per package using an input-specified discount rate. Supporting tables show summaries of emplacement descriptions, rock logistics, waste operations logistics, and backfilling logistics.

3.5 OFFICE OF CRYSTALLINE REPOSITORY DEVELOPMENT (OCD)

Northeast Granite Regional Environmental Characterization Studies (DB-30-40-01 - 80459)

Objectives are 1) to prepare an environmental characterization of the Northern Appalachian and Adirondack Crystalline Region comprised of portions of the states of Connecticut, Maine, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, and Vermont and 2) to prepare an analysis for and recommendations of areas within that region that are suitable candidates for more detailed environmental characterization.

Summary

This program has developed an environmental characterization data base for all or parts of nine (9) Northeast and New England states under the sponsorship of the Office of Crystalline Repository Development (OCD). A draft Environmental Characterization Report (ECR) was transmitted to each of the states examined within the study.

Technical Progress

The project is managed by the OCRD's Site Characterization Department and is a component of NWTs's (DOE) repository site-selection process as outlined in DOE's Confidence Rulemaking Statement. Major efforts in FY 1983 have been directed toward 1) responding to OCRD and/or DOE comments on the preliminary drafts of the characterization document and 2) distribution of a draft in May to the nine states for their review and comment.

Highlights for the second half of the fiscal year are as follows:

- The ECR was modified as a result of comments made by EG&G, and then transmitted to OCRD on April 14. EG&G was contracted

by DOE Chicago to serve as an independent (internal) reviewer of the six characterization reports being prepared for DOE (and OCRD).

- Project staff attended a review meeting in Columbus, Ohio, on April 19, where final changes were proposed by EG&G before publication of the ECR.
- A Records Turnover Package was transmitted to Dames and Moore during May containing key resources used in development of the ECR. Dames and Moore will be carrying on the environmental characterization work in the Northeast next fiscal year.

As of the end of FY 1983 no public comments had been received on the ECR. PNL concludes its three-year effort on this program at the end of FY 1983.

4.0 LOW-LEVEL WASTE MANAGEMENT

The objective of the Low-Level Waste Management Program is to develop the technology to dispose of low-level radioactive wastes in a manner that protects the public health and safety.

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4.0 LOW-LEVEL WASTE MANAGEMENT

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4.1 SPECIAL WASTE FORM LYSIMETERS - ARID (AP-05-20-15 - 80749)

The primary objective of this task is to conduct waste-form leaching tests in a field facility in order to determine typical source terms generated by commercial solidified low-level waste. The solidification agents to be tested are cement and polyvinyl styrene. Through field and laboratory research, the chemical and physical processes that control the concentration of radionuclides in the soil solution surrounding the waste in an arid climate will be identified. Methods for representing source-term boundary conditions in radionuclide transport models will be determined.

Summary

The Special Waste Form Lysimeters - Arid Task was begun in FY 1983 and is scheduled to be completed in FY 1987. There is a similar task ongoing at the Savannah River Laboratory for a humid climate. A site for the new lysimeter facility has been selected and approved, the necessary environmental and safety assessments have been addressed, and construction has proceeded to the point where waste installation can begin. The field test facility is scheduled to become fully operational during the second quarter of FY 1984.

Negotiations with staff from Brookhaven National Laboratory (BNL) have been completed for the procurement and delivery of the waste samples. BNL has procured two of ten waste samples and completed analyses of

one of the raw stream samples. The remaining samples for field and laboratory analyses are to be shipped to PNL in FY 1984. Samples will be obtained that are as close as possible to those obtained for the Savannah River Laboratory lysimeter program.

The geochemical computer code to be used on this program has also been selected and deficiencies in the thermodynamic data base identified. Work to upgrade the model to better suit the needs of this task is scheduled for FY 1984.

Lysimeter Study

The Special Waste Form Lysimeters Study is designed to quantify the release and migration of radionuclides from solidified commercial low-level waste. A field test facility has been built to contain selected waste forms in specially constructed lysimeters. Field leaching tests will be conducted on actual commercial waste forms obtained from BNL. Waste forms tested will include material from power reactor waste streams that have been solidified in cement and Dow polymer. The waste form will be characterized by standard laboratory tests such as MCC-1 and the IAEA leach test to obtain estimates of radionuclide release. Solubility studies will also be conducted to determine the amount of contaminant available for transport after release. Data collected from this research will be used to

relate laboratory measurements of waste form characteristics to the release and migration rates observed in the field. Comparisons will be made between results obtained for this arid site facility and those from the humid site located at Savannah River.

The major construction activities at the field test facility have been completed. Figure 4.1 shows the cut-away and top view of the test facility; Figures 4.2-4.4 are photographs of the facility during the various phases of construction. The commercial waste materials are to be removed from the 55-gal drums in which they are shipped and then placed in the 10-ft-deep, 6-ft-diameter, closed-bottom lysimeters. A

central caisson (Figure 4.1) will provide access to the individual lysimeters for selective sampling and to the instrumentation. The lysimeters will be backfilled with soil so that at least 3 ft of material covers the top of the waste drum. The soil material will provide radiological shielding as well as a medium for sorption of soluble radiochemicals that may leach from the waste forms. Suction candles (ceramic cups) placed in the bottom and around the waste drums will be used to periodically collect soil solution for chemical analysis. Moisture content and temperature of the soil surrounding the waste form will be monitored periodically; radiological

FIGURE 4.1. Engineering Drawing of Special Waste-Form Lysimeter Test Facility

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FIGURE 4.2. Early Construction Phase: Pouring of Concrete Around the Lysimeters

analyses will be performed in situ and through selective sampling.

BNL has completed the analyses of one of the waste stream samples and the solidified form of this waste. The additional waste stream samples and waste forms will be analyzed and shipped to PNL in FY 1984. After the facility is operational in the first quarter, the site will be closely monitored for signs of radioactive release from the waste samples. If any release is detected, then soil and soil solution samples will be collected for analysis. Analytical chemis-

try will include analysis of macro- and trace elements using inductively coupled plasma emission spectroscopy (ICP) and atomic adsorption (AA) techniques. Anions will be analyzed using ion chromatography (IC) and radionuclides by low-level gamma and x-ray counting techniques. This will provide the Low-Level Waste Management Program with direct field results regarding leach and migration rates from actual commercial solidified waste.

In addition to the field monitoring, which is the central purpose of the task, a

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FIGURE 4.3. Construction of Lysimeter Facility Prior to Backfilling

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FIGURE 4.4. Status of Lysimeter Facility at End of FY 1983.
Facility backfilled and ready to receive waste forms.

series of laboratory testing and geochemical modeling exercises is planned. These tests will help to predict expected leach rates and help to interpret the field data. The ion speciation-solubility and mass transfer geochemical code MINTEQ will be used to model the waste stream, waste form and any column effluent and batch solutions. Based upon FY 1983 efforts, four elements have been identified as important to add to the MINTEQ thermodynamic data base for a thorough geochemical modeling effort to be completed. Those elements for which the thermodynamic data are lacking or incomplete in the MINTEQ thermodynamic data base are cerium, cesium, antimony and cobalt. A June 1984 letter report will describe the data evaluation process used and the constants accepted for the reactions. Based on this evaluation of data, the need for solubility experiments to fill gaps in the thermodynamic data will be determined. Specifically, the goals of the laboratory and modeling work will be to identify which mechanisms are controlling the release of radioactivity from the waste form.

4.2 TRANSPORT ASSESSMENT - ARID (AR-05-15-15 - 80033)

The mission of this program is to provide the required technology for use in monitoring radionuclide transport through geohydrologic systems. This technology will assist in the assessment of the safety of buried solid low-level radioactive waste.

Summary

- Task Summary Report. A topical report was prepared that summarizes the research efforts of the Transport Assessment - Arid task from its inception in 1977 to the present time. It relates these ef-

forts to the technology needs for shallow-land burial of radioactive wastes and emphasizes the need for reliable models to predict long-term performance.

- Model Verification. Model verification studies were initiated to test the reliability of water-flow models for predictions of water balance at arid sites. Experimental data sets from the Buried Waste Test Facility (BWTF) were compiled that document the measurements of climate variables (precipitation, temperature, humidity, wind speed) and changes in soil moisture storage over a period of 1 year (April 1979 - April 1980). Agreement between model results and experimental measurements was found satisfactory using both an isothermal and nonisothermal flow model and testing model results against measured values of annual moisture storage and drainage.
- Transpiration Studies. Transpiration studies were conducted documenting the influence of vegetation on moisture storage and drainage on coarse soils at Hanford. Results to date indicate that as much as 20% (>5 cm) of the precipitation drained below the root zone at a grass-covered site. Model simulations are planned that are designed to demonstrate the sensitivity of the water balance to changes in soil type and plant cover as well as frequency and timing of precipitation.

Task Summary Report

The task summary report documents PNL research activities related to water and radionuclide transport under arid, shallow-land burial site conditions. This effort has been ongoing since FY 1978. In the

report, technology needs at arid-zone sites are summarized. The unique features of arid site, shallow-land burial for radionuclide waste disposal are explained. The report emphasizes the importance of the interaction among climate, soil, plants, engineered barriers and the buried waste at an arid site. Justification is given for detailed modeling of unsaturated flow and transport for the long-term assessment of shallow burial sites in arid climates, and key results are given of initial characterization and monitoring at a field test site at Hanford.

Model Verification Studies

The Transport Assessment - Arid task is emphasizing the evaluation of water-flow models. The flow of water at a waste disposal site is controlled by the five processes of 1) infiltration, 2) redistribution, 3) drainage, 4) evaporation, and 5) transpiration. A water-flow model is made up of submodels that describe each process either individually or in groups as shown in Figure 4.5. Also shown in Figure 4.5 are the major input parameters needed to execute the various studies for

each of the models listed in the figure.

The Darcian model describing infiltration, redistribution, and drainage, together with the evaporation models, was evaluated during FY 1983. The transpiration models shown in Figure 4.5 will be examined in FY 1984.

A major step in verifying the model is the compilation of experimental data sets that illustrate the processes shown in Figure 4.5. A data set was compiled to illustrate transpiration and evaporation. The data set for evaporation now complete, was compiled from water balance experiments conducted at the BWTF from mid-1978 through 1982. Field experiments that will provide the transpiration data set were started in January of 1983 and will continue through FY 1984.

The data collected from the BWTF have been compiled, and detailed moisture profiles from four lysimeters, two 1.5 m (5 ft) deep and two 7.6 m (25 ft) deep, have been used for water balance studies using data collected from May of 1978 through 1982. The water balance studies consisted of monitoring soil water content, drainage, soil temperature, and climatic variables while

FIGURE 4.5. Models Available to Describe Processes Controlling Water Flow

half the facility was receiving natural precipitation only and half was receiving extra irrigation. The lysimeters were kept bare of vegetation, except for one weighing lysimeter in FY 1983. Although data from the latter cannot be used to illustrate transpiration, they do illustrate the processes governed by the Darcian model as well as evaporation.

The data set included irrigated and non-irrigated plots. Irrigation was applied from May 1979 to October 1980 at a rate of twice the natural precipitation. This raised the total water applied to the irrigated lysimeter to three times ambient during this 1.5-yr period. Total water added to the irrigated lysimeter during the 4.5-yr experimental period was about twice that received by the unirrigated lysimeter. The amount of water stored in the two lysimeters was equal before irrigation, and the amount of water stored in the irrigated lysimeter increased during the period of irrigation. After irrigation was stopped, the excess water drained out of the lysimeter and the water stored in each lysimeter was equal again.

After the first year, we observed deep drainage from the lysimeters receiving natural precipitation as well as irrigation. Also, the drainage rate at 7.6 m is equal to that at 1.5 m, indicating that in unvegetated soil there is no upward movement from this depth. During our first year of monitoring a vegetated site to collect transpiration data, we have also seen evidence of deep drainage below the root zone. These data refute a commonly held assumption that no deep drainage exists at arid sites.

Simulation of drainage curves represents an important test for the water-flow models being evaluated. Drainage at the 1.5- and

7.6-m levels is representative of water draining from the trench cap into the waste zone and deep drainage out of the waste zone. These data are also expected to show the importance of the evaporation model to predicating water flow deep in the profile. The predictions of drainage at the 1.5-m level are expected to be more sensitive to the choice of the evaporation model than the drainage predictions for 7.6 m. The deep-drainage predictions are expected to be most sensitive to the hydraulic conductivity estimates used in the Darcian model.

The final data set used to evaluate the models consists of the water content profiles measured in the lysimeters throughout the life of the BWTF. Water content was measured monthly at several depths in each lysimeter. The water content in the irrigated lysimeter increased significantly ($>1.3\%$) over the water content of the unirrigated lysimeter. Water contents measured after irrigation was stopped show that the water content in the irrigated lysimeter decreased to levels equal to those measured in the unirrigated lysimeter. This reaction to the irrigation was also observed in the water storage data. Simulation runs covering a 1-yr test period (April 1979 - April 1980) with both isothermal and nonisothermal flow models were compared and found in reasonable agreement with the experimental data. Additional testing is planned to evaluate the sensitivity of the models to precipitation distribution and soil hydraulic properties.

Transpiration Studies

Results of nearly 1 yr of intensive field measurements have shown that drainage below the root zone exceeded 5 cm (20% of the annual precipitation) for a wet year (August

1982 - July 1983) at a grass-covered site at Hanford. Although average rainfall at Hanford is seldom above 15 cm/yr, the study-year precipitation exceeded 26 cm, with above-normal precipitation occurring in all months except May and August. The early season rainfall increased soil moisture content throughout the 3-m profile. Moisture content changes, measured at depth with a downwell neutron probe, indicated that significant drainage occurred below the root zone of the grass-covered site. Measurements of plant root distribution suggested that most of the grass roots were confined to the top of 30 cm. No roots were found below 1 m. The large amount of drainage from this arid site is attributed in part to the shallow root zone and to the soil, which is a well-drained sand and nearly homogeneous throughout the top 3 m. These observations appear to be the first documented evidence of significant recharge from grass-covered areas at Hanford. Plans are under way for simulation of unsaturated water flow using site characteristics that include measured soil properties, plant cover, root distribution, and measured climatic variables. We are convinced from field data that drainage can be a significant component of the water balance at an arid site, particularly if the rainfall occurs during periods of low potential evaporation and if the soil is coarse-textured and uniform with depth. For optimal design of low-level waste sites, modifications of plant cover and soil type can be shown through model simulation to be effective in significantly reducing drainage.

4.3 VERIFICATION INSTRUMENT DEVELOPMENT (AR-05-15-15 - 80334)

The objective of this research program is to organize, apply, and develop, as required, instrumentation for assaying the radionuclide content of waste packages received by land burial operators, both to verify the data provided by the generator/shipper and to provide the most accurate records possible of buried materials.

Summary

The final report of the program, Instrumentation and Assay Procedures for Verification of the Radionuclide Content of Low-Level Waste Packages, PNL-4848, was issued in September 1983.

Several standard 55-gal drums have been fabricated in Dow modified vinyl ester binder using Dow Chemical Company proprietary procedures. These standards are available for instrument calibration, and the author should be contacted to make arrangements for borrowing them or for nonproprietary details of the fabrication process. These barrels each have a single radioisotope homogeneously distributed throughout the matrix. Concentrations are approximately 10 mCi/m³ for ⁶⁰Co, 10 mCi/m³ for ⁹⁰Sr, 14 mCi/m³ for ¹³⁴Cs, 15 mCi/m³ for ¹³⁷Cs, and 10 nCi/g for transuranic alpha activity.

To provide complete calibration capabilities for all low-level waste package assay instrumentation, it will be necessary to prepare standards in all conceivable package configurations, in a wide variety of matrix densities, and for each radioisotope identifiable in the unknown packages. Practically speaking, however, packages should be confined to 30 and 55-gal drums and 4 x 4 x 8-ft

boxes, and a few different matrices such as Dow modified vinyl ester binder and Portland cement should suffice.

4.4 MOBILITY OF ORGANIC COMPLEXES OF RADIONUCLIDES IN SOILS (AR-05-15-15 - 81034)

The objective of this project was to develop and employ standard procedures for evaluating how and to what extent organic complexants affect the mobility of low-level waste radionuclides in soils.

Summary

Experimental studies were concluded and a final report (PNL-4796, Mobility of Organic Complexes of Nickel and Cobalt in Soils by J. L. Swanson) was issued. Excerpts of this report were used to prepare a paper (PNL-SA-11533, Mobility of Organic Complexes of Radionuclides in Soils) for presentation at the Fifth Annual DOE LLWMP Participants' Information Meeting.

The results discussed both in earlier reports by Swanson (1981 and 1982) and PNL-4796 contain examples of different effects of organic complexants on radionuclide mobility. In no case studied was the radionuclide mobility decreased by the complexant. The complexant had little or no effect in some systems, but in most cases the effect was one of increased radionuclide mobility. Great differences, however, were observed in the magnitude of the enhanced mobility, and it is this magnitude that should be of prime concern. It makes no difference to public health and safety if a complexant increases the distance traveled by a radionuclide from 0.1 to 10 m, for example, if it must travel 1000 m to reach the accessible environment.

The increase of the mobility caused by a complexant depends on both the magnitudes of the formation constants of the complexes with the radionuclides and the soil-derived elements and also on the rates of the complex formation and dissociation reactions and the rate of ground-water movement. It depends also on whether the complexes themselves are sorbed by the soil.

The magnitude of the enhanced radionuclide mobility also varies widely among radionuclides, complexants, and soils. The radionuclides present in low-level wastes are largely defined by the normal operations of the nuclear industry. The organic complexants currently present in low-level wastes are largely defined by current industry practices, but changes could perhaps be made rather simply. This is especially true if some complexants were required to be destroyed or packaged more rigorously before the wastes could be disposed, while others could be disposed without special treatment. The kinds of soils present in low-level waste disposal sites will probably vary from site to site, and some soils are more tolerant of organic complexants than others.

Regardless of the relative magnitudes of organic complexant-enhanced radionuclide mobilities in soils from different sites, other site-specific data are also important. For instance, a site having soil that results in a large complexant-enhanced mobility could still be a preferred site if the ground-water flow is sufficiently low. A mobile species will not move unless there is water to transport it.

Soil characteristics at a site that retard complexant-enhanced mobility of radionuclides include the following:

- high radionuclide sorption capability (K_d) and capacity (loading)

- large quantities of elements that form highly stable complexes with the complexants present in the waste
- presence of materials that result in rapid attainment of the various equilibria involving the complexants, the radionuclides, and the soil-derived elements.

For waste disposal the most desirable characteristic of a complexant is that it rapidly equilibrate with the radionuclides and the soil-derived elements. If all equilibria are attained rapidly, complexant-enhanced mobility of radionuclides should be minimal because of a low free-complexant concentration resulting from dilution by the ground water and from competition for the complexants by the elements present in the soil. Radionuclide mobility could be much more severe with kinetically inert complexes, which may migrate through some soils at the same speed as the ground water or which may be sorbed by other soils in a pseudo-equilibrium situation.

Another desirable characteristic of the complexants is that the constants for the formation of complexes with radionuclides not be too high; that is, a high concentration of free complexant would be required to lower the K_d value to an unacceptable level. Still another desirable characteristic is instability under environmental conditions, especially if the complexant degrades to materials that are not complexants themselves.

An ideal low-level waste disposal site would be one from which absolutely no water migrates; there could thus be no migration of radionuclides regardless of the presence of organic complexants. This is, of course, not practically achievable in the real world. However, it is likely that a number

of combinations of site-specific and complexant-specific factors such as those just discussed, together with the water migration rate, will give radionuclide mobilities that are acceptably small even in the presence of complexants. The work done on this project helps to identify such satisfactory combinations of factors.

4.5 GROUND-WATER TRANSPORT MODEL DOCUMENTATION AND EVALUATION GUIDELINES (AR-05-15-15 - 80635)

This program will develop standard guidelines for the documentation and evaluation of ground-water transport models to be applied to low-level waste management.

Summary

Guidelines are being developed to assist potential users in selecting appropriate computer codes for ground-water contaminant-transport modeling. They are to aid managers with selecting predictive models for evaluating either arid or humid low-level radioactive waste burial sites.

Evaluation test cases in the form of analytical solutions to fundamental equations and experimental data sets have been identified and recommended to ensure adequate code selection, based on accurate simulation of relevant physical processes. The recommended evaluation procedures will consider certain technical issues related to the present limitations in transport-modeling capabilities. A code-selection plan will depend on identifying problem objectives, determining the extent of collectible site-specific data, and developing a site-specific conceptual model for the involved hydrology. Code selection will be predicated on steps for developing appropriate systems model.

Introduction

This report summarizes work accomplished during the past 2 years, FY 1982-1983 and describes the final ground-water transport modeling guidelines. The guidelines deal in general conceptual terms with ground-water transport modeling methodology and are not meant to give specific advice on the best design of a burial site. Models designed to evaluate environmental transport are the main concern.

Model Selection Approach

An early conclusion drawn while developing the guidelines was that a generic systems modeling approach would not be adequate for performing accurate transport predictions, which are needed for environmental impact assessments. Generic systems models are useful for preliminary site evaluations; but generally they do not include adequate mechanistic complexity for describing all important physical processes acting in both humid and arid sites. Moreover, the wrong physical processes are sometimes emphasized.

A potential user usually can not merely select an appropriate model from a "display shelf" of fully developed models. The appropriate model must always be developed by selecting codes consistent with a conceptual model of a specific site. All too often users attempt to force-fit a problem into a familiar yet inappropriate code. Thus selection of a transport code should actually be an active process of model development, as outlined in the steps below.

Transport Model Development Steps

1. Identify site and define study objectives.
(Define problem-solving objectives.)

2. Collect and analyze site characterization data.
3. Formulate site conceptual model. (Identify important physical processes acting. Make conceptualization consistent with study objectives.)
4. Identify appropriate equations for physical processes. (Complexity conforms to conceptual model.)
5. Select computer codes to solve process equations. (Code documentation study guides selection.)
6. Interface selected codes to form systems model. (Selected codes must be compatible.)
7. Evaluate code performance. (Verify and validate when necessary. Apply relevant test cases.)
8. Test assembled systems model with site-specific data. (Test simulation of individual component processes for site-specific parameters.)
9. Decide to accept or reject systems model. (Repeat development steps if model not satisfactory. Additional data may be needed to modify conceptual model.)

The development of a conceptual hydrologic model, which guides the code selection, depends on the study objectives and the extent of available site-characterization data. Selected codes should be compatible with the complexity of the conceptual model. The level of detail required to describe fundamental physical processes involved will generally indicate the appropriate form of mathematical theory. Commonly, code selection is viewed as simply choosing the most general equations and most powerful numerical methods. This view is incorrect. A conceptual model is perhaps the most important aspect that determines modeling results. And any adequate numerical method may be employed

with proper accuracy control. Equations representing the appropriately detailed mathematical theory should dictate the selection of relevant computer codes or the modification of available ones.

Selected codes are then interfaced to form the systems model. Clearly, selected codes to be interfaced must deal with compatible variables. For example, every ground-water solute transport model should consist of three parts for: water flow, convective-dispersive solute transport, and chemical-media interaction. The three parts may be integrated into one code, but often each is described by separate codes which must communicate and exchange calculations through interfacing. The interfacing determines the process coupling of those parts.

A key step during development of the systems model is an evaluation to ensure that selected codes properly simulate the involved physical processes. Code evaluation requires testing to ensure that numerical accuracy and proper physical process representation is achieved. Assurance comes from good code documentation or direct preliminary simulation testing. It can never be assumed that a code which operates well with one parameter set will work equally well with another. That must be proven for each code application. Such evaluation establishes a model's scientific credibility, relative to basic assumptions about the system.

Test cases in the form of analytical solution codes and experimental data sets are used to evaluate a systems model. Analytical solutions to fundamental equations test the numerical accuracy of code algorithms, and experimental data sets help ensure that physical behavior is properly described. Analytical solutions can also be used to estimate model parameters from more basic site data.

A central thesis of the guidelines is that adequate evaluation test cases must take into account current technical issues on ground-water transport modeling. These issues express limitations on current physical theories and modeling capabilities. Only by keeping those issues in mind can a user truthfully assess a model's predictive accuracy and establish credibility in applications.

Together with formulating guidelines, this project's main technical contribution, therefore, has been to identify technical issues regarding ground water and to select evaluation test cases.

Guideline Development Progress

Progress achieved has mainly been reported in four unpublished letter reports communicated to EG&G and Oak Ridge National Laboratory. Contents of those reports, however, are being included in the final guidelines, to be completed in November 1983.

The first report, April 1982, explained why a generic systems modeling approach would not be adequate for accurate transport prediction. That conclusion was supported by a review of an example systems model for shallow-land burial (Lester et al. 1981).

A second letter report, August 1982, gave a preliminary description of the proposed guidelines. It also identified major technical issues that must be resolved during model development. Merely selecting the most general code can not bypass those issues, since they determine how a code should be applied to analyze a problem. Some of those issues are related to site-modeling requirements; use of simple versus complex computer codes; required degree of model coupling; dimensionality of physical representation; employed

numerical methods; assumed initial and boundary conditions; effects of model calibration and parameter uncertainty sensitivity; and appropriate spatial and temporal scales. Modeling results will ultimately depend on a user's treatment of those technical issues. Perhaps only simplified generic systems models, which are not realistic or accurate, would eliminate the influence of a user's interpretation. Therefore guidelines for model selection and evaluation would appear to be a better alternative.

The third letter report, October 1982, identifies a selection of analytical solutions for test cases. Specific computer codes, identified below, consisting of collections of analytical solutions to basic equations for various initial and boundary conditions were made operational and test-run on a PNL DEC computer. The solutions cover cases for saturated and unsaturated, steady and transient water flow, and solute transport including chemical retention, as well as coupled species transformation. Radioactive chain decay transport is also described. The analytical solutions were identified according to the basic physical processes they describe. The following analytical solutions were made operational for: saturated ground-water flow (Cleary and Ungs 1976, Dagan 1964), unsaturated zone flow (Warrick et al. 1981, Perroux et al. 1981), solute transport (Cleary and Ungs 1976; van Genuchten and Alves 1982; Yeh 1982), and solute transport with chemical retention and transformation (van Genuchten 1981 and 1982).

The fourth letter report, April 1983, which identified some experimental data sets for model evaluation purposes, also discussed the previously listed model development steps. A finding was that aquifer (saturated zone) and unsaturated zone test cases call

for different levels of complexity. Realistic aquifer experimental test cases are usually too complicated for easy comparison. But saturated flow theory is well established and self-validating when a ground-water model is implemented for a specific application. This is a result of hydrology-specific calibration that must be performed for each aquifer simulation. On the other hand, unsaturated zone modeling includes many incompletely understood phenomena that must be examined through experimental observations. Moreover, there are often many different mathematical descriptions of the same unsaturated zone physical process. That makes actual experimental data indispensable for evaluating simulation of individual processes. Furthermore, calibration data for an unsaturated zone are usually not available when a site is first studied.

Besides identifying many analytical and experimental test cases in the open literature, several specific test cases, indicated below, were implemented. Such cases are not to be considered as benchmark tests, but only to be used to gain confidence in a related code's range of ability.

- Unsaturated zone examples of Hillel (1977) were simulated and verified with a PNL code. These cases represent the basic processes of drainage, infiltration, and evaporation in a soil profile.
- An accurate test code called INFILID, for unsaturated infiltration under constant surface flux conditions, was developed based on the method of Perroux et al. (1981). The code better represents rainfall infiltration instead of the usual ponding condition. Accurate numerical simulation of infiltration is a common technical issue.

- Special attention was given a three-dimensional experimental dispersive transport example by Sudicky and Cherry (1979). That tracer data demonstrated the consequences of variability of ground-water flow velocity within a shallow sandy aquifer.
- The technical issue of non-Fickian and scale-dependent dispersive transport for coupled chemical species was studied in conjunction with the INTRACOIN (1982) radionuclide transport code comparisons.
- To treat that dispersion issue, a new one-dimensional stochastic transport code SICHAIN was developed. The code demonstrates how field-scale dispersion can be described without resorting to a sometimes inappropriate diffusion representation, which may give incorrect physical behavior.

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5.0 REMEDIAL ACTION

The objective of the Remedial Action Program at PNL is to support the Department of Energy's Uranium Mill Tailings Remedial Action (UMTRA) Project. The aim of UMTRA is to provide remedial actions at 25 inactive uranium mill sites, and associated contaminated vicinity sites, to stabilize and control the tailings to the extent that radiological and nonradiological hazards from them do not exceed EPA standards for the protection of the public health, safety, and the environment.

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5.0 REMEDIAL ACTION

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5.1 RADON BARRIER SYSTEMS FOR URANIUM
MILL TAILINGS (AH-10-15 - 80379)

The overall objective of this program is to develop radon barrier systems that will meet Environmental Protection Agency standards, minimize the use of remedial action, and remain stable for a very long period, including development of supporting technology and engineering specifications.

Summary

- Successful site-specific asphalt/aggregate radon barrier formulations have been developed for the Grand Junction, Salt Lake City, Rifle, Durango and Riverton sites.
- Candidate earthen cover materials were tested for compactability and moisture retention. Radon diffusion coefficients were determined on five pit run materials at two compaction densities.
- Pit run materials exhibited radon diffusion characteristics similar to native soils and non-stony sediments.
- Long-term moisture was estimated from water-retention characteristics measured at 15 bar. Compacted soils had moisture saturation levels ranging from 0.25 to 0.95 at 15 bar-water contents, indicating a dependence of the moisture saturation on the fines (<200 mesh) in the soil material.
- A simple correlation was developed that relates moisture saturation (at a given site) to the annual evaporation and precipitation at a given site and the percent of fines in the sample (as an index of the capacity of the soil to hold water. The correlation has yet to be tested for all UMTRAP (Uranium Mill Tailings Remedial Action Program) sites. Effects of increased gravel and stone content alters the moisture and density relationships sufficiently that the correlation may need to be modified if stony or rocky soil material is used.
- A summary of research on surface stabilization was prepared that presents significant results and guidelines for designing long-term protective covers.
- Radon flux measurements made during June on the Grand Junction Field Test site show that average radon fluxes for all the covers tested are less than the corresponding averages measured in October 1982. All 1981 covers were less than 20 pCi/m² sec.
- Two earthen covers and five different asphalt covers were cored to provide samples for characterization and analysis at PNL. Moisture and density measurements were made on the earthen cover cores. Samples were also used for radon diffusion coefficient measurements.
- An area of bare Grand Junction tailings 9 by 9 m was monitored for radon flux and cored to provide data for verification of the source-term calculation procedure.

The tailings from the cores were measured for radium, emanating power, radon diffusion coefficient, moisture density, and particle-size analysis. These values were used to calculate the radon source term for the tailings to be compared to other measured flux values. Calculated fluxes were within 50% of the measured values.

Asphalt Covers

Formulation Analysis

The purpose of this task was to develop asphalt/aggregate formulations for five high-priority sites--Salt Lake City, Grand Junction, Durango, Rifle, and Riverton--using locally available materials. Aggregates were obtained from near the five sites, and Petroleum Sciences, Inc., developed the formulations using asphalt obtained from Conoco in Denver, Utah Emulsions in Salt Lake City, and Bituminous Materials in Albuquerque.

The formulations all had 22 wt% asphalt as a dry aggregate basis and met the specifications for radon barrier systems developed in 1982. The concrete sands used as aggregates worked well although in some cases it would have been desirable to have more fines in the aggregate. The Salt Lake City and Durango aggregates were the most difficult for which to develop good formulations.

Radon diffusion tests showed that good seals were obtained for all the formulations. Radon diffusion coefficients for the samples are shown in Table 5.1.

Long-Term Moisture Equilibrium

Measured radon diffusion coefficients for candidate earthen cover samples indicate that radon flux can be reduced and the required cover thickness decreased when compacted soil is used for a radon cover system. The reduced radon flux is attributed largely to the greater water-retention capabilities of compacted soils. Table 5.2 shows moisture content and calculated and measured diffusion coefficient results from five test materials at several compactions. Computed radon diffusion coefficients were within a factor of three of the measured values. The average ratio of measured to computed diffusion coefficient was 1.2. The results suggest that pit-run materials yield diffusion coefficient values similar to uniform, non-stony soils. The data further suggests that the empirical relationship relating radon diffusion to moisture saturation holds for most soils and earthen materials that would be available for use at UMTRAP sites. Figure 5.1 compares the measured diffusion coefficients for the compacted pit-run materials with the computed values for non-stony, uniform soil materials.

TABLE 5.1. Diffusion Coefficients for Asphalt/Aggregate Radon Barriers

<u>Aggregate Source</u>	<u>Asphalt Source</u>	<u>Diffusion Coefficient,</u> <u>cm²/sec</u>
Grand Junction	Conoco	5.3×10^{-5}
Salt Lake City	Utah Emulsions	1.7×10^{-4}
Durango	Bituminous Materials	2.6×10^{-5}
Rifle	Conoco	6.1×10^{-5}
Riverton	Utah Emulsions	1.8×10^{-5}

TABLE 5.2. Radon Diffusion Coefficients for Selected Earthen Cover Materials Compacted to Various Proctor Densities (ASTM-1557D) and Equilibrated at 15 Bar Water Contents

Sample	Bulk Density, g/cm ³	% Proctor Density	Water Content, dry wt%	Moisture Saturation	Radon Diffusion Coefficient, cm ² /sec	
					Measured	Computed
Durango-shale	1.88	95	12.4	0.77	9.3E-4	1.4E-3
	1.73	87	10.7	0.52	6.2E-3	9.8E-3
Salt Lake-pit	1.92	91	5.3	0.35	3.2E-2	1.9E-2
	1.86	89	4.0	0.24	4.1E-2	2.9E-2
Grand Jct-pit	2.00	97	6.5	0.50	2.6E-2	9.6E-3
	1.88	91	9.3	0.57	5.0E-3	6.9E-3
Grand Jct-adobe	1.88	91	11.1	0.69	1.4E-3	3.1E-3
	1.84	89	14.4	0.83	4.0E-4	7.4E-4
Grand Jct-shale	1.89	95	15.0	0.95	2.8E-4	1.0E-4
	1.79	90	15.7	0.83	3.0E-4	7.6E-4

FIGURE 5.1. Radon Diffusion Coefficient Prediction from Field Moisture in Earthen Covers

The agreement is satisfactory; the average measured/computed ratio is 1.2 for the ten pit-run samples tested. Also compared are the wide range in the diffusion coefficients and moisture saturation of the pit-run material and the relatively narrow range of diffusion coefficients measured for noncompacted

native soils. The data suggest that compaction significantly increases the moisture saturation range and concurrently produces a range of lower radon diffusion coefficients than those found in uncompacted native soils.

The uncertainty in the measured radon diffusion coefficient for soil materials shown

in Figure 5.1 cannot be overemphasized. Figure 5.2 shows how this uncertainty (a geometric standard deviation of ± 2.5) in estimating or measuring the radon diffusion coefficient can affect cover thickness estimates. The cover thickness required to meet the EPA 20 $\text{pCi m}^{-2}\text{sec}^{-1}$ standard on a tailings site with a bone surface flux of 300 $\text{pCi m}^{-2}\text{sec}^{-1}$, is plotted as a function of cover bulk density.

Even soils with high moisture contents exhibit high uncertainties (factor of two) in cover thickness requirements at moderate to low densities. Although compaction is a

desirable feature for radon control, it severely inhibits root growth. A site requiring vegetation for long-term stabilization probably will require at least 1 m of uncompacted surface soil. Placing the moist-compacted soil at depth will also aid in preventing long-term desiccation or de-densification of the compacted zone. The final cover design at a vegetated site will probably be a two-layer cover system with the plant root zone located in uncompacted soil, with the compacted layer, radon barrier located below the root zone. A similar cover design has proved effective at the Grand

FIGURE 5.2. Earthen Cover Thickness Required To Reduce Radon Flux to 20 $\text{pCi m}^{-2}\text{sec}^{-1}$ as a Function of Soil Bulk Density and Moisture Content

Junction field site where compacted layers are located more than 1 m below the surface. All three compacted earthen cover systems at this site have continued to perform well and at present meet the EPA radon guidelines.

The long-term moisture in an earthen cover is a function of climate (precipitation and potential evaporation), plant cover (actual evapotranspiration), soil type, and depth to the water table. A simple relationship has been developed that expresses the soil's ability to store water in terms of physical properties such as the amount of fine (<75- μ m particles). This relationship does not take into account variations in soil mineralogy, organic matter content and chemical properties of the solid, but assumes that most materials used for radon control covers will be subsoil materials low in organic matter with mineralogy and chemistry that do not significantly affect the radon attenuating properties of the cover. The 75- μ m soil fraction is reasonably well correlated with the amount of water held by a soil at 15 bars pressure. This size fraction is a commonly measured parameter, used in engineering to separate sand and "slime" fractions of tailings materials. Although the 75- μ m fraction is a crude estimate, it is an improvement in previous attempts to correlate soil texture with long-term moisture in earthen cover systems.

The proposed correlation is:

$$M_r = 0.124 P^{1/2} - 0.0012E - 0.04 + 0.156 f_c$$

where M_r = residual soil moisture (saturation ratio)

P = annual precipitation

E = annual evaporation

f_c = soil fraction passing a 200-mesh sieve.

Cover density can be increased significantly over normal field densities by use of heavy compacting equipment. However, if vegetation is used to stabilize the cover, at least a 1-m loose-packed topsoil of suitable quality is recommended to establish and maintain plant growth on the cover. Tightly compacted and wetted subsoil materials can be used effectively as radon control layers in a two-layer cover system. Water contents at 15-bar pressures can be used to estimate the lower limit of moisture saturation under typical cover conditions.

Rocky soil can change the relationship of long-term moisture saturation by increasing the overall soil bulk density and moisture saturation levels. The two samples tested from pit-run materials taken from Grand Junction and Salt Lake City contained over 50% material >#10 (2 mm) sieve. Typical field densities of 1.6 of gravel or stones. This increased density gives rise to decreased total porosity (0.40 to 0.24 cm^3/cm^3), resulting in increased moisture saturation levels (0.23 to 0.51). Soil tests must account for rock/stone content to accurately predict radon diffusion.

Long-Term Stabilization

Surface Stabilization

Covered tailings are comprised of components that function together as a system. Surface covers protect this system from erosion that could damage its integrity. Surface covers interact with other system components through soil moisture, plant root growth, and burrowing activities of animals. The UMTRAP research on surface stabilization addressed questions about the effects of surface cover on soil moisture and biotic

intrusion and about the interactions between radon barriers and surface covers.

Although each tailings pile will require an individual design, three basic cover designs involving vegetation were identified (Figure 5.3): A) vegetation alone, B) vegetation in combination with surface

rock, and C) vegetation in combination with subsurface rock. One or all of these may be used on a given tailings pile, and if gully or channel erosion is probable, rock riprap may be added. The vegetation material consists of various combinations of plant types (grasses, forbs, and shrubs) that are adapted

FIGURE 5.3. Basic Cover Designs Using Vegetation

to the conditions at a particular site. Rock material can range from pit-run to sorted material (engineered rock armor designs were not considered in UMTRAP research but are a part of an ongoing NRC project).

The inactive tailings sites in the West (Figure 5.4) were grouped into three major geoclimate regions to evaluate the adequacy of vegetation for long-term stabilization: the Colorado Plateau, the West Slope of the Rocky Mountains, and the Northern Great Plains. Four general vegetation types were found at Western sites: grasslands, shrub-steppe, salt-shrub, and woodland. Soil-loss rates calculated using the Universal Soil Loss Equation, were variable within geoclimatic regions and vegetation types, but trends

were apparent. Vegetation or vegetation plus a layer of surface rock provides adequate stabilization against long-term average soil loss for slopes less than 10% at the UMTRAP sites evaluated. However, detailed analyses of erosion due to severe storm events, gully formation, and channel cutting is necessary for each site.

Radon barriers and the trifluralin herbicide used as a root barrier had no significant effects on vegetative cover or soil moisture. Root distributions were not significantly affected by the asphalt seal or by the herbicide. No damage to the asphalt seal due to root penetration was detected. Root penetration into tailings occurred in an area without the asphalt seal.

FIGURE 5.4. Location of Inactive Uranium Mill Tailings Piles

The effects of surface rock on vegetation and soil moisture was determined by: 1) simulation modeling, 2) a lysimeter experiment, and 3) field-scale studies. Results indicate that care must be taken when designing surface covers. The moisture dynamics of the tailings pile can be altered significantly by surface treatment. Vegetation covers and combination vegetation and rock covers can result in a relatively stable moisture content. Rock covers that exclude plant growth, even for short time periods, can increase the moisture content of the tailings pile/cover, and may lead to drainage.

Surface rock affected vegetation structure by preferentially favoring the growth of plant species during the first growing season. Weedy species had higher cover values on rock treatments while seeded perennial species had higher values on soil without rock. The use of surface rock may compromise the favorable perennial vegetation for the doubtful added protection of a rock cover. Additionally, some rock covers may result in increased gully erosion.

Regardless of the surface cover design used, efforts to establish vegetation are necessary, especially in the West. Establishment of vegetation in arid areas is typically episodic, depending on favorable soil moisture conditions. The more arid the site, the more infrequently favorable conditions occur naturally. Seeding and irrigating properly during the first growing season can create favorable conditions for plant establishment. Relying on natural succession to establish vegetation could leave the surface without a perennial plant cover for considerable lengths of time (conceivably tens of years).

A means to quantify erosion stresses likely to impinge upon a tailings pile is

critical for designing long-term protective covers. A survey of available erosion models was conducted, and various models and approaches to using them were suggested. However, regardless of the model used to predict erosion, implementation and interpretation of results must be based on a thorough knowledge of geomorphological processes. Criteria for estimating future climatic conditions need to be defined because all erosion models are highly sensitive to climatic variables.

An approach to designing surface covers, presented in the form of a decision tree (Figure 5.5), outlines the process of gathering information and evaluating the effects of the surface cover on the containment system. Three phases are recognized: assessment, preliminary and final design. The benefit of an approach such as this is the flexibility it allows in designing covers.

Engineering Specifications

Materials and Application Specifications

The purpose of this task was to develop materials and application specifications for asphalt emulsion radon barrier systems. These specifications are detailed in a topical report Asphalt Emulsion Radon Barrier Systems - An Overview of the Technology. The report includes also a summary of laboratory and field tests, seal stability studies, and cost estimates for asphalt covers.

To determine the optimum time to compact an asphalt/aggregate seal, five identical admix samples were compacted at different times. Delays ranged from 3 to 30 days after mixing. There was little variation in the density of the material or the diffusion coefficient. The density ranged from 1.7 to 1.8 g/cm³. The diffusion coefficients were

FIGURE 5.5. Decision Tree for Designing Inactive Mill Tailings Surface Covers

all on the order of 10^{-5} . This indicates the seal can be compacted as soon as the free water separates from the admix, usually within the first 1 or 2 days.

In June of this year samples were taken from the 1979, 1980, and 1981 test plots. Visual inspection of the samples revealed no deterioration of the seals. Radon diffusion tests were made with five different samples. Samples of the seals applied with a cold-mix

paver had radon diffusion coefficients of $2.2 \times 10^{-4} \text{ cm}^2/\text{sec}$ (1980 test plot) and $7.0 \times 10^{-5} \text{ cm}^2/\text{sec}$ (1981 test plot). The samples from the soil stabilizer plots had diffusion coefficients of $8.0 \times 10^{-4} \text{ cm}^2/\text{sec}$ (1979 test plot) and $4.0 \times 10^{-4} \text{ cm}^2/\text{sec}$ (1980 test plot). A sample of rubberized asphalt cement applied in 1980 had a diffusion coefficient of $4.3 \times 10^{-5} \text{ cm}^2/\text{sec}$. All five systems are still effective radon barriers.

Field Test Monitoring

Site Visits

A monitoring trip was made to Grand Junction, Colorado, June 13-30, 1983. The site was monitored for radon flux, moisture and density profiles, radon-concentration profiles, and general site maintenance.

Radon-flux monitoring of the Grand Junction site included the 1981 asphalt, 1981 earthen cover, 1981 column tests, 1980 cold-mix paver, 1980 rubberized asphalt, 1980 in situ asphalt, and 1979 in situ asphalt test areas. Table 5.3 provides a summary of the results of the measurements along with the October 1982 monitoring results for comparison.

As can be seen in Table 5.3, the average radon flux for each cover is less in June than the corresponding average measured in October 1982. The exact cause of this decrease is not known at this time, but the decrease seems to be associated with the summer season. The same decrease in flux was observed also in June 1982.

In addition to the large-scale tests, radon-flux measurements were made on several of the column tests located at the south end of the earthen cover test plots. The radon flux values for these measurements are presented in Table 5.4.

Source Characterization

The source characterization task comprised both laboratory and field studies. The laboratory studies include radon diffusion coefficient measurements on tailings and earthen covers along with measurements of radium and emanating power on the same materials. The field studies include measurements on tailings and earthen covers in the field to verify calculation methods for the source-term characterization. Tailings samples from several UMTRAP sites were measured for ^{226}Ra content and emanating power to get an idea of the variability of these values between the UMTRAP sites. A summary of the measurements is shown in Table 5.5.

An experiment was performed at the Grand Junction tailings pile in June to learn

TABLE 5.3. Grand Junction Radon Flux Values for October 1982 and June 1983

Test Area	June 1983, $\text{pCi m}^{-2}\text{sec}^{-1}$			October 1982, $\text{pCi m}^{-2}\text{sec}^{-1}$ Average ^(a)
	Range	Average	Standard Deviation	
1981 asphalt	0.00-6.55	0.76	1.27	0.9 ± 1.0
Mancos shale	0.10-2.37	0.90	0.84	1.7 ± 1.2
Bentonite clay	2.24-19.7	6.80	5.10	11.3 ± 7.2
Compacted adobe	0.73-6.79	4.77	3.33	9.8 ± 5.4
Uncompacted adobe	2.59-15.9	6.46	5.48	28.4 ± 18.3
1980 asphalt CMP	0.11-3.27	0.51	0.61	
Hot rubberized asphalt	2.10-11.8	5.38	4.10	
1980 in situ	6.20-80.3	29.2	29.5	
1979 in situ	6.90-31.5	15.4	10.3	

(a) Plus or minus 1 standard deviation.

TABLE 5.4. Radon Flux Values for Grand Junction Column Tests

Column	June 1983, $\text{pCi m}^{-2}\text{sec}^{-1}$			October 1982,
	Range	Average	Standard Deviation	$\text{pCi m}^{-2}\text{sec}^{-1}$ Average ^(a)
Mancos shale	4.17-18.8	8.21	7.05	19.1 ± 7.7
Bentonite clay	2.20-24.0	11.1	9.55	15.6 ± 8.4
Compacted adobe	10.2-30.9	17.1	9.64	38.8 ± 10.8
Uncompacted adobe	55.5-176	97.9	74.2	40.3 ± 8.6
Bentonite/lime	1.47-2.33	1.90	0.61	4.6 ± 1.4
Admiral's test 10'	-	223	-	-
Admiral's test 14'	-	134	-	-

(a) Plus or minus 1 standard deviation.

TABLE 5.5. ^{226}Ra and Emanating Power Measurements on Uranium Mill Tailings from Selected UMTRAP Sites

Location	^{226}Ra , pCi/g	Emanating Power, %
Ambrosia Lake	115	5.7
Falls City	288	18.3
Falls City	300	11.5
Grand Junction	803	18.9
Monument Valley	40	24.7
New Rifle	352	36.2
Old Rifle	826	25.6
Shiprock	402	13.9
Salt Lake City	621	32.3
Tuba City	433	20.0
Average $\pm$ Std. Dev.	418 ± 264	20.7 ± 9.3

whether the source term (radon flux) from the tailings can be calculated from the physical and radiological properties of the tailings. Twenty-five centimeters of overburden was removed from an area 9 by 9 m on the tailings pile. The tailings were allowed to equilibrate for several days and then radon flux measurements were made on five locations over a 3-day period using the PNL flowthrough radon flux measurement system. The tailings were cored at the five locations using 7.1-cm Shelby tubes. The tailings samples were

bagged and shipped to PNL for radium, emanating power, bulk density, moisture particle size, and diffusion coefficient analysis. A summary of the measurements for each core hole is shown in Table 5.6. The measured parameters of the tailings were used to calculate the radon flux from the tailings using an equation reported by Strong and Levins. The equation is:

$$J = 10^4 \text{ Ra E } \rho \sqrt{\lambda D}$$

TABLE 5.6. Characteristics of Grand Junction Uranium Tailings Cored During June

Hole	^{226}Ra pCi/g	Emanating Fraction	Bulk Density, g/cm ³	Moisture, g/g	Diffusion Coefficient cm ² /sec
SCNW	352.9	0.399	1.31	0.0469	0.0135
SCNE	324.7	0.268	1.55	0.0368	0.0163
SCC	374.3	0.326	1.44	0.0452	0.0260
SCSW	440.6	0.310	1.42	0.0432	0.0131
SCSE	358.7	0.299	1.37	0.0468	0.0194

where Ra = radon content, pCi/g

E = emanating fraction

ρ = dry bulk density, g/cm³

D = diffusion coefficient, cm²/sec

λ = decay constant for ^{222}Rn , sec⁻¹

10⁴ = conversion from pCi m⁻² sec⁻¹

The calculated flux values were then compared to the radon fluxes measured before coring in June 1983 over the locations of the core samples. The results of the comparison are shown in Table 5.7.

As can be seen from Table 5.7, the calculated radon fluxes are consistently higher than the fluxes measured over the 3-day period in June 1983. There also seems to be a systematic error involved in the measurements made with the small tents as they are over a factor of two lower than the fluxes measured

with the large tents. The cause of this error is not known at present. The differences between the calculated fluxes and those measured with the large tents can be attributed to the fact that the equation used to calculate the radon flux does not take into account the influences of advective transport of radon. Others (Rogers et al. 1983) have shown that over a short period transport can account for differences as large as a factor of two or more over that expected from diffusion of radon alone. This is substantiated by the results of 2 years of monitoring at Grand Junction, which has shown a seasonal variation in radon flux of at least a factor of two. Therefore, it can be concluded, at least for one area on the Grand Junction tailings pile, that a simple diffusion equation can be used to predict radon fluxes based on

TABLE 5.7. Comparison of Calculated and Measured Radon Fluxes for Grand Junction, pCi m⁻²sec⁻¹

Site	Average Calculated Flux	Average Measured Flux	% Difference
SCNW	323.5	212.2*	52.5
SCNE	258.1	226.8*	13.5
SCC	410.3	109.3**	275
SCSW	333.2	233.2*	42.9
SCSE	308.1	101.4**	203

* Measured with large area tent (0.929 m²).

** Measured with small area tent (0.581 m²).

the physical and radiological properties of the tailings. The accuracy of the prediction will depend on the accuracy of the individual measurements of each property of the tailings. The uncertainty is likely to be quite small for parameters such as radium content, moisture, and bulk density but larger for parameters such as diffusion coefficient and emanating fraction, which are highly moisture dependent.

References

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5.2 LINER EVALUATION FOR URANIUM MILL TAILINGS (AH-10-15 - 80395)

The objective of this program is to evaluate the effectiveness of prospective lining materials for preventing moisture transport of radionuclides and hazardous chemicals from uranium mill tailings over long-term periods.

Summary

All programmatic requirements for the Liner Evaluation for Uranium Mill Tailings Program have been completed. Relevant technical contributions have been compiled by Buelt et al. (1983) in a final report published in September. The most recent technical accomplishments included the completion of the asphalt aging studies and the sampling, analysis, and evaluation of the asphalt and clay liners installed in field in 1981. Study results showed the expected performance lifetime of the asphalt liner to be greater than 1000 yr with extremely slow, but meas-

urable, degradation reactions. The clay liner, although more permeable, is an effective chemical and radionuclide contaminant barrier via its natural sorptive behavior as the leachate passes through the liner.

Asphalt Aging Studies

Buelt and Barnes (1983) published a report describing the results of the asphalt aging studies. The results showed that the lifetime of the catalytic airblown asphalt as an effective leachate barrier for inactive uranium mill tailings is greater than 1000 yr. This is determined by infrared spectrometric analysis of asphalt samples aged in specially constructed exposure columns. Infrared spectrometry identifies the carbonyl-containing components, which are the reaction products of aging reactions. With time, the carbonyls normally combine with other long-chain asphalt molecules that increase the viscosity and hardness, making the asphalt more prone to brittle fracture.

This study successfully demonstrated that the aging of asphalt (formation of carbonyls) could be accelerated by increasing temperatures and oxygen concentrations. According to reaction-rate measurements, the imposed temperature and oxygen concentrations produced an equivalent aging effect of 7 yr over a 3-month period. Increased acidity concentrations, however, were determined to have an unmeasurable effect on aging.

Aging reactions during the 3-month exposure were limited to a penetration beyond the exposed asphalt surface of only 10 to 40 μm . This amounts to only 0.1 to 0.5% of the total membrane thickness. Since the penetration and rate of carbonyl formation is so small, the asphalt's expected performance lifetime is more than 1000 yr.

Feed Liner Studies

The asphalt and clay liners installed in the Grand Junction tailings pile in 1981 have been sampled and evaluated to determine their effectiveness in the field. The results of these evaluations have been published by Buelt et al. (1983) in the final report.

General Performance

It was apparent during sampling that the moisture blocks indicated accurately the saturation levels of the foundation soils beneath the liners. Under the clay liner, which gave consistently high moisture readings, the soil was extremely wet--almost muddy. This is because the clay liner is more permeable; its attribute as a liner is its enhanced retardation potential for mobile contaminants. Under the asphalt liner, where most indicators read low levels of saturation, the foundation soil was almost bone-dry. At one location only, near the center of the asphalt pit, the readings were higher (60 to 100% saturated); this was confirmed by observing the foundation soil at that location. The soil under this portion of the liner was wetter because of an apparent faulty installation. Whereas the asphalt liner was consistently 0.7 to 0.9 cm thick at most sample locations, a thin spot was observed at this location because insufficient asphalt was applied. This left a couple of 1-cm holes in the membrane, accounting for the higher moisture here. This experience underscored importance of quality assurance in installation.

Asphalt Liner Performance

After removal from beneath the tailings in Grand Junction after 2 years' exposure, the

asphalt liner samples contained unusually high readings of β - γ emitters (2000 - 4000 dpm). Portions of these samples were submitted for gamma-scan analysis to determine whether the radionuclides are on the surface of the asphalt or absorbed in the membrane. Results of the gamma-scan analyses of various asphalt samples showed little detectable radium and no evidence of other radionuclides. The fact that the activity had disappeared by the time samples were analyzed 3 weeks later can be explained only by the presence of radon. Apparently radon was sorbed into the asphalt liner or its surrounding moisture and decayed within the 3-week period. The radon was probably concentrated at the liner due to decay of ^{226}Ra in the tailings beneath the liner's foundation soil.

In addition to these analyses, visual comparisons were made between the field samples, virgin samples, and laboratory-aged samples according to a procedure identified by Geir and Morrison (1968) for asphalt membranes. The observations were used to determine the following:

- statistical variation of membrane thickness
- thickness of crust formation on exposed surface
- extent of soil impregnation from foundation soil support.

As mentioned earlier, one of the three field samples had thin spots due to nonuniform coverage of the asphalt during application. This sample earned a fair to poor rating, primarily because of its discontinuity. The other two samples achieved a good rating with very few surface cracks, a thin layer of crust (1 to 8%), good flexibility, and no physical damage. The laboratory-aged samples were similar in all respects. The virgin sample, which was removed from the

decrease is apparently due to a slow dissolution by the solvent with time. Increasing the concentration of noble metals in the base solution did not appear to significantly affect the recovery fraction.

According to the ORNL patent (Campbell and Buxton 1981) on sugar denitration for noble metal recovery, palladium is precipitated by adding sugar to strong acid solutions of spent nuclear fuel reprocessing waste. We conducted tests similar to those described in the patent. In these tests, we varied the amounts of sugar added to portions of the simulated PUREX and commercial base stock solutions. Sugar was added periodically to these solutions, and the solutions were maintained at a refluxing temperature of 100°C. In the first test, solutions were adjusted to 3N and 10N nitric acid. After reaction and cooling, the solutions were filtered, and the filtrates and precipitates were recovered for analysis. Quantitative analyses of the precipitates have been difficult, and we have been unable to close our material balance. Qualitatively, however, palladium was identified in the precipitate in sufficient quantity to ensure that some of it could be recovered during reprocessing, but rhodium and ruthenium have not been identified in the residue.

In order to overcome the known analytical problems, the tests were repeated using alternative filtration procedures in which a filter composed of mixed esters of cellulose acetates and nitrates was substituted for one

of ashless filter paper. Only solutions adjusted to 3N nitric acid were used. In one test, the total amount of denitration sugar was increased from 16 g to 32 g, and the quantity of precipitate increased substantially. Analysis of the precipitates and filtrates is in progress.

Screening tests similar to those for the amine-borane resins have also been conducted with activated carbon embedded with chelates that are specific for noble metals. The chelates used are dimethylglyoxime for palladium and phenylthiourea for rhodium and ruthenium. Analyses of the supernatants by ICP indicate that both chelates removed substantial amounts of palladium.

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field after installation in 1981, was in excellent condition with no surface cracks and no evident crust formation.

The results show that installation practices are critical to good performance of the asphalt membrane as a liner. The comparison also supports the results of laboratory aging, which demonstrated that the aging reactions are confined to the exposed surface and do not penetrate well within the membrane.

Clay Liner Performance

Six cores 10 cm in diameter were sampled from the clay liner to determine the amount of contaminant breakthrough and the liner's permeability. Permeability measurements ranged between 10^{-9} and 10^{-7} cm/sec and were achieved by the strong swelling properties of the bentonite in the liner material. Analy-

ses by ion-coupled plasma and x-ray fluorescence of the tailings, liner material, foundation soil, and their leachates show that radionuclide mobility is very low through the liner material. The fact that the tailings have been neutralized at Grand Junction also contributes to the low mobility of contaminants.

References

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6.0 SUPPORTING STUDIES

The objectives of the Waste Management Supporting Studies are to provide support to DOE's Office of Civilian Radioactive Waste Management and conduct environmental impact studies and analysis of public and institutional issues.

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6.0 SUPPORTING STUDIES

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6.1 HANFORD DEFENSE WASTE STUDIES - DEVELOPMENT OF ENGINEERING AND ENVIRONMENTAL INFORMATION (AR-05-10-02Z - 80381)

The objective is to assist DOE-RL in developing and assessing methods for the disposal of existing and future Hanford radioactive defense wastes.

Activities During Reporting Period

Work performed during this reporting period is summarized as follows:

- schedule preparation
- project scoping activities
- preparation of plans and logistics for Hanford peer review of Rockwell Engineering and PNL Environmental Analysis Data
- post-disposal scenario analyses.

A brief description of each activity follows.

Scoping Activities

PNL participated in and provided input to ten scoping sessions convened by DOE-RL. The scoping sessions were held for the purpose of developing consensus on a reference plan for disposal of certain defense wastes to be analyzed.

Offsite Peer Review

Plans were initiated for peer review of the Engineering and Environmental Impact Data by the staff of DOE Field Offices and DOE Contractors and by independent reviewers.

Post-Disposal Scenario Analysis

A study for determining potential impacts to in-place stabilized waste sites at Hanford by glaciation and glacial flooding was begun and completed during this reporting period. The study was conducted through M. G. Foley, Department of Geosciences Research and Engineering at PNL, by Dr. R. C. Craig, Department of Geology, Kent State University, Kent, Ohio. A final report was received in September.

An extensive revision of PNL draft report Natural and Human-Induced Events and Release Scenarios for Hanford Defense Waste was completed. Review of the draft report was begun. Further revisions are currently anticipated.

6.2 HANFORD DEFENSE WASTE STUDIES - PREPARATION OF AN ENVIRONMENTAL IMPACT STATEMENT (AR-05-10-02Z - 80754)

The objective is to assist DOE-RL in the preparation of a draft and a final Environmental Impact Statement for existing and future Hanford radioactive defense wastes.

Activities During Reporting Period

Work performed during this reporting period is summarized as follows:

- preparation of responses to public comments following publication of the Notice of Intent

- preparation and revision of the EIS Implementation Plan
 - EIS schedule preparation
 - DEIS scoping activities
 - review of EPA proposed standards
 - preparation for and participation in EPA Hanford Site visit
 - preparation for and participation in meetings with DOE-HQ, SRL, and DOE-Albuquerque
 - preparation of plans and logistics for Hanford peer review of the HDW-DEIS
 - preparation of plans for offsite peer review
 - preparation of draft chapters for the comment draft EIS (DEIS).
- A brief description of each activity follows.

Responses to Public Comments

Responses were prepared to 18 letters submitted to DOE-RL by individuals, state and Federal agencies during and following the NOI comment period. The letters were considered in the preparation of the HDW-EIS implementation plan (IP). Letters and DOE responses were included as an appendix to the IP.

EIS Implementation Plan

The implementation plan for preparing the HDW-EIS was prepared and then revised several times following review by DOE-RL and DOE-HQ/DP and GC. A workshop meeting was held at DOE-HQ on August 5 to obtain final HQ input and approval of the IP and to discuss the EIS preparation schedule, as well as DOE-HQ and DOE-RL interactions. Approval for the IP was granted by DOE-HQ on August 22, 1983.

EIS Scoping Activities

PNL participated in and provided input to ten scoping sessions convened by DOE-RL. The

scoping sessions were held for the purpose of developing consensus on a reference plan for disposal of certain defense waste addressed in the HDW-EIS. The detailed scoping paper issued by DOE-RL, was used in the preparation of the HDW-EIS implementation plan.

Review of EPA Proposed Standards

Concentrated efforts continued during this reporting period on the review of proposed EPA standard 40 CFR 191. The intent here was to determine potential impacts of the proposed standard on the preparation of the EIS. The joint DOE/PNL/RHO review resulted in the EPA presentation during a visit by EPA officials to the Hanford Site described below.

EPA Hanford Site Visit

A concentrated effort was made in preparations for the EPA staff visit to the Hanford Site during October. PNL reported on the status of the EIS, scope of defense wastes to be considered, scope of alternatives and scope of environmental impacts. An approach to performance assessment of in-place stabilized waste sites was also included. PNL provided detailed input to DOE-RL that may be proposed for the revision of EPA's proposed standard for implementing in-place stabilization of Hanford Defense Waste. This effort is expected to continue into the next reporting period.

DOE-HQ and Field Office Visits

PNL participated in presentations and discussion with DOE-HQ and Field Office staff to 1) obtain insight into the experience gained by these staff in preparation of the Defense Waste Processing Facility (DWPF-DOE/EIS 0082)

and the Waste Isolation Pilot Plant (WIPP-DOE/EIS 0026) Environmental Impact Statements; 2) to provide overview of the status, scope and schedule of the HDW-EIS; and 3) to solicit reviews by and through the DOE and contractor staff. Staff from SRL visited Hanford during July and staff from DOE-RL, PNL and RHO visited DOE-HQ and DOE-Albuquerque during August.

Hanford Peer Review

Plans were prepared to ensure periodic peer review of the HDW-EIS program. An overview committee, directed by C. M. Unruh of PNL, and a technical review committee were formed. The overview review committee, consisting of senior staff from PNL and RHO, convened during August and provided verbal and written comments during and following the review. Review was provided by the technical review committee after each of the HDW-DEIS comment draft materials was completed.

Offsite Peer Review

Plans were begun for peer review of the HDW-DEIS comment draft by DOE Field Offices and DOE Contractors staff, independent reviewers, and National Academy of Sciences staff. At DOE-RL's request, PNL made telephone and written contacts with DOE Field Offices staff and independent reviewers. DOE is to contact NAS staff.

Comment Draft HDW-EIS

Cesium and strontium capsule data submitted by Rockwell in September were used to prepare draft materials for HDW-DEIS Chapters 3 and 5 (Description of the Alternatives and Description of Impacts, respectively).

Chapter 4 (Description of the Environment) was drafted and submitted for PNL review and comment.

6.3 WASTE MANAGEMENT SYSTEM STUDIES

(AP-05-20-10 - 80219)

Decision making in the selection, development, and implementation of waste repositories and supporting technologies requires supporting analyses and independent assessments of alternatives to provide guidance on the most appropriate courses of action. To assure a balanced evaluation, the analyses and assessments must be performed on a systems basis. This program performs such studies.

Technical and Economic Evaluations

Most of the analyses planned for FY 1983 were completed, and work started on preparation of a summary report discussing the results. A few RECON computer code runs were yet to be completed and some additional calculations may have to be done to resolve questions that develop during the drafting of the report.

Four waste treatment alternatives have been considered and their impact on waste management system costs evaluated in a system utilizing a basalt repository. All treatment alternatives include solidification of HLW as borosilicate glass. They include:

1. Package TRU (transuranic) wastes without treatment.
2. Compact the hulls and general process trash.
3. Compact the hulls and noncombustible trash, incinerate combustibles, and immobilize the ash and scrubber solution and fluorinator fines with cement.
4. Melt the hulls and failed equipment, compact remaining noncombustibles, incinerate combustibles and immobilize with cement.

A conceptual integrated waste processing center separate from the reprocessing plant (based on modified Allied General Nuclear Services [AGNS] concepts) has been described for each of these alternatives.

Some preliminary conclusions developed in these analyses include:

1. Substantial facilities will be required for assaying TRU and SNM (special nuclear materials) content of TRU wastes and for waste package inspection and certification of compliance with the assumed repository acceptance specifications.
2. A basic waste treatment facility with no TRU waste treatment but including high-level waste (HLW) vitrification, working inventory storage, and the assay, inspection and certification facilities may cost in excess of \$250 million (1983).
3. Possibly 30 to 40% of this could be saved by integrating waste treatment with the reprocessing plant during design and construction.
4. TRU waste treatment will add only about 10 to 20% to the waste processing center costs.
5. Without TRU waste treatment for volume reduction, repository costs may be as much as 30% higher for reprocessing wastes compared to spent fuel (assuming rod consolidation).
6. Repository costs for reprocessing wastes can be reduced to comparable or lower levels than spent fuel repository costs with hulls compaction or melting. However, total system costs, i.e., treatment, transport, and repository, still exceed spent fuel system costs.
7. Government financing of reprocessing waste treatment would apparently reduce reprocessing waste system costs below spent fuel system costs.

8. Co-emplacement of remote-handled TRU wastes with HLW in the repository, either with or without volume reduction, achieves relatively small savings--on the order of \$0.1 billion out of \$4+ billion for a 70,000-MT repository.
9. A long-lived overpack requirement for TRU wastes would add on the order of \$1 billion for a 70,000-MT repository.

Repository Cost Model Development (RECON)

The objective of this task in FY 1983 was to broaden and enhance RECON model capabilities to address three current key repository design issues: alternative emplacement methods, co-emplacement of wastes, and receiving and packaging facilities.

Progress during the reporting period on these tasks is summarized as follows:

- A letter report entitled "Improving Waste Handling - Building Cost Estimating Capability," dated August 15, 1983, was submitted to DOE-RL.
- A letter report entitled "Pillar Emplacement Logic Development Task for the Repository Cost Model Development Project," dated December 20, 1982, was submitted to DOE-RL.
- A letter report entitled "Developing Co-emplacement Analysis Capability," dated March 31, 1983, was submitted to DOE-RL.

Special Issues Analyses

The objective of this task in FY 1983 was to respond on a case-by-case basis to special requests for analysis of a special technical or interface issue of concern to the Division of Repository Development. During the first half of FY 1983, PNL responded to two such requests. One concerned draft guidance to the sites regarding waste

acceptance specifications, and the other concerned a system cost study plan for the National Waste Terminal Storage (NWTs) program.

A presentation was given at HQ on April 20, 1983, on the NWTs Program Waste Management System Cost Studies Plan developed under this task. We were advised to do nothing further with this plan until comments from DOE, if any, are received. These two tasks consumed the funds budgeted for this activity in FY 1983.

During the second half of the fiscal year no work was performed under the Special Issues Analyses task.

Nuclear Fact Book

The objective of this task in FY 1983 was to update PNL-4239 in a timely fashion to reflect developments significant to DOE's nuclear waste management program plans. This objective was achieved with the publication of Nuclear Fact Book, PNL-4239 Edition 2, dated May 1983. In developing this edition, particular attention was given to those aspects having impact on DOE's waste repository deployment plans, such as the enactment, in January 1983, of the Nuclear Waste Policy Act. The new edition also contains an additional section on sociopolitical aspects.

PNL-4239 Edition 2 was distributed to about 90 DOE officials. Twenty-seven copies were sent to the U.S. DOE Technical Information Center (TIC) to satisfy requests from non-DOE personnel. The TIC copies can be obtained at a cost of \$17.50 each.

PNL has received a variety of requests from non-DOE persons and entities requesting multiple copies of the book. These include

the Atomic Industrial Forum, the American Nuclear Energy Council, the American Nuclear Society, and some DOE contractors. We told them they could get copies from TIC.

In August, PNL received a letter from Harwood Academic Publishers (HAP) requesting a loan of the camera-ready manuscript of the Nuclear Fact Book Edition 2. HAP's intent is to publish this material worldwide. PNL requested DOE-RL to advise us as to an appropriate response. Subsequently, DOE-RL authorized PNL to loan the originals to HAP.

Public Information Analysis

The objective of this task in FY 1983 was to structure a public information program aimed at:

1. increasing public understanding of waste management technology and programs
2. correcting public misconceptions about certain aspects of nuclear waste storage and disposal
3. assisting DOE in successfully interfacing with the communities in potential disposal site areas.

Work on this task during the reporting period culminated with the submission to DOE-RL of a letter report entitled "Waste Management System Studies Public Information Task, Task 2 Report," May 1983.

6.4 NUCLEAR MATERIALS TRANSPORTATION TECHNOLOGY STUDIES

6.4.1 Thermal Analysis Methods (AR-05-25 - 80746)

The objective of this research is to provide improved analytical methods for thermal analysis of shipping casks.

Summary

During FY 1983 a Joint Thermal Structural Codes Information Exchange Meeting was held with representatives of government and industry. Thermal and structural code benchmarking activity was presented. Several benchmarking problems were defined and presented to industry for benchmarking of industry-used codes.

Some preparations were made for the upcoming workshop in FY 1984 in which details of the results of the benchmarking problems will be presented and additional benchmarking and thermal and structural phenomena will be discussed.

6.4.2 Structural Analysis Methods (AR-05-25 - 80747)

The objective of this research is to provide a survey of analytical structural methods applicable for the design and licensing of spent fuel shipping casks. Structural computer code benchmarking is being used in the performance of this survey.

Summary

In FY 1983 an information exchange meeting was hosted in which both structural and thermal codes relevant to spent fuel shipping cask design were discussed. The meeting was attended by government and industrial representatives interested in cask design and licensing.

Structural Analysis of Casks

In previous reporting periods for this program, several computer codes potentially useful for structural analysis of spent fuel shipping casks were identified and acquired. These codes were available to the public ei-

ther as source forms or on a fee-for-use basis. The codes have been benchmarked using simple cask-like models. A series of germane structural response parameters has been selected and tabulated so that the codes could be compared in a consistent fashion.

During FY 1983 an Industrial/Government Joint Thermal and Structural Codes Information Exchange meeting was held. Information on the structural code benchmarking and a similar thermal code benchmarking activity was presented. The information exchange meeting was hosted by the Transportation Technology Center, Sandia Laboratories, Albuquerque, New Mexico.

6.4.3 Nuclear Materials Transportation Studies Criticality Research (AR-05-25 - 80745)

The objective of this research is to obtain experimental criticality data in support of the design and safe operation of nuclear fuel transportation systems.

In previous reporting periods, existing experimental data and the near-term requirements for data to establish a consistent, firm and complete data base for verifying criticality calculations were identified. In coordination with Sandia Laboratories staff and members of the Nuclear Energy Agency (NEA) Working Group assessing the reliability of criticality calculational techniques, a series of experiments has been planned and designed to fulfill some of the near-term needs for data by providing data in support of the NEA international benchmarking efforts. These initial experiments are designed to simulate conditions created in transport systems and high-density fuel storage racks by the practice of using sleeves or canisters containing strong

thermal neutron absorbers around the fuel elements for criticality control. Such arrangements create very effective neutron flux traps in which nonthermal neutrons escaping the absorber sleeve are thermalized and thus "trapped" outside the sleeves enclosing the fuel elements. The effectiveness of these flux traps to maintain a given degree of subcriticality is very sensitive to the amount of water between the absorber sleeves, the amount of absorber, and the location of the flux trap.

The experiments have been divided into five sets of measurements such that the effects caused by varying a single parameter can be observed for use in verifying calculations in a stepwise fashion. In this manner the ability of a calculational technique to reproduce the stepwise change can be determined, and the masking of compensating errors in the calculations can be minimized. The measurements have been identified as TTC-1 through TCC-5. TTC-1 and TCC-2 provide data for use in verifying calculations to assess the effect on criticality if for some reason the subcritical spacing between fuel element canisters is not maintained. TCC-3 provides similar data on the effect caused by a loss, or absence, of neutron absorber used in the canister for criticality control. TCC-4 provides data on the effect that loss of absorber has on the neutron multiplication factor, k_{eff} . TTC-5 is an attempt to provide data on the theoretical model, Problem 5, used by the NEA Working Group in their recently completed exercise of intercomparison and validation of criticality computational methods. Fabrication of TTC-1 components is in progress, and experiments with this assembly are scheduled to begin in February 1984.

6.4.4 Nuclear Materials Transportation Characterization (AR-05-25 - 80744)

The objective of this research program is to develop the models and data required for estimating shipping requirements and costs for all major categories of defense and commercial nuclear waste, and waste packaging alternatives.

A logistics code has been developed at PNL to analyze the interaction of the various facilities within the nuclear waste disposal system. This program tracks spent fuel discharges (historic and projected) from a given reactor fuel basin through a series of facilities that includes Federal interim storage (FIS), fuel reprocessing plants (FRP), monitored retrievable storage (MRS), and mined geologic disposal (MGD). The characteristics of the inventory at each facility during any given year are available from the analysis. Most of the input supplied to the logistics analysis comes from the DOE Spent Fuel Data Base currently being maintained at PNL.

The Characterization of Spent Fuel To Be Shipped to a Disposal Site

The logistics model utilizing both historic and projected discharges was used to analyze the characteristics of spent fuel to be shipped to a proposed MGD facility or facilities. Various scenarios were employed to provide a range of anticipated values. Cases were analyzed for both a single MGD facility and a dual MGD facility system. The single-facility system assumed operation in 1998 with a capacity of 70,000 MTU of spent fuel. The dual-facility system assumed a second MGD facility in 2002 adding another 70,000 MTU spent fuel capacity. Two cases were run with two different delivery schemes. The first case assumed that spent fuel would

be shipped directly from the various reactor fuel basins to the MGD facility or facilities on a strictly oldest-available basis. The second case scheme accounts for events that will occur at various reactor sites that will supersede the oldest-available logic. These events are delineated in the Nuclear Waste Policy Act (NWPA) and include the following:

1. FIS must be emptied within 3 years of the start of operations of the MGD facility.
2. Reactors exceeding full core reserve (FCR) in a given year will be given higher priority in shipping.
3. Reactors that terminate in a given year will be given higher priority in shipping.

The second case assumes that the first reactors exceeding their FCR margins will ship fuel to the FIS. This amount is limited to 1900 MTU total by the NWPA. Reactors exceeding FCR margins after receipt of 1900 MTU at FIS but before the opening of the MGD facility are assumed to provide additional "at-reactor storage." Once the MGD facility begins operation, the spent fuel to be delivered to the facility will follow the logic presented above.

Analytical results for the various cases show that a single MGD facility using oldest-fuel-available logic will receive about 2 to 3% of its receipt rate in excess of the current design basis of 1.2 kW/MT. The single MGD facility using event-priority logic shows an increase to about 10 to 12% of its receipt rate in excess of current design. The addition of a second MGD facility, in 2002, utilizing either oldest-available logic or event-priority logic shows that greater than 50% of the spent fuel to be shipped to an MGD facility will exceed the current design basis after about 2015.

6.5 KRYPTON ION IMPLANTATION

(AS-25-05 - 86116)

The objective of this program is to develop the process of implanting krypton in a sputter-deposited metal matrix for the ultimate storage of krypton-85. Pilot-scale demonstration of the process, using nonradioactive krypton, and small laboratory-scale tests using krypton-85 will be conducted.

Summary

The need for reliable, easily maintainable power supplies combined with current-control circuits for the krypton implantation process makes it advisable to evaluate several engineering approaches. The major effort in the search for the most appropriate solution to the control of electrical arcs associated with the process is connected with the high-voltage target power supply circuit. Three approaches are being evaluated: one developed by PNL and two by commercial manufacturers. The two commercial power supplies have been ordered, with early 1984 delivery schedules. The PNL-developed unit is presently being evaluated with the aid of an arc-simulation unit specially constructed for this purpose.

Safety and environmental considerations dictate that release of ^{85}Kr be minimized during storage. Thus krypton-release behavior from a $\text{Ni}_{0.81}\text{La}_{0.09}\text{Kr}_{0.10}$ alloy has been studied under various temperature and chemical environments. These studies include release of krypton from the alloy in both the crystalline and amorphous states while in a vacuum, release while exposed to 166 torr of oxygen, and release while exposed to room temperature and 90°C water. In addition, the expansion behavior of this alloy and of a $\text{Ni}_{0.82}\text{Y}_{0.11}\text{Kr}_{0.07}$ alloy has been

studied in an effort to explain the spallation that has occurred during deposition of thicker layers of NiLaKr.

The release of krypton from this alloy in vacuum or in 166 torr oxygen is projected to be less than 1% in 10 years at any temperature 300°C or below. The release from this alloy when immersed in water is projected to be up to 3.5% in 10 years.

Storage of $\text{Ni}_{0.81}\text{La}_{0.09}\text{Kr}_{0.10}$ at temperatures greater than 200°C would result in a significant rate of crystallization to a body-centered cubic structure. During this transformation if the temperature is below 400°C the krypton release rate will decrease markedly.

Thermal expansion data show that krypton-containing alloys can either expand or contract during heating. While heating to 300°C the $\text{Ni}_{0.81}\text{La}_{0.09}\text{Kr}_{0.10}$ alloy contracted by nearly 0.3% and then began to expand, whereas the $\text{Ni}_{0.82}\text{Y}_{0.11}\text{Kr}_{0.07}$ alloy expanded continually while heating to 300°C. During isothermal treatment at 300°C the $\text{Ni}_{0.82}\text{Y}_{0.11}\text{Kr}_{0.07}$ alloy expands irreversibly by less than 0.2%.

Equipment Development

The krypton immobilization program based on implanting krypton gas in a growing sputter-deposited film requires a reliable control circuit integrated with a high-voltage target power that can promptly extinguish electrical arcs believed to result from hot cathode spots on the surface of the sputtering target. In addition, the circuitry must restore the voltage to the target as quickly as possible without breaking into an oscillatory mode. To minimize the electric power requirements for the immobilization process, it is desirable that the power supply/limiter combination operate as efficiently as possi-

ble. The most important feature for this unit is reliability/maintainability. Similar devices are also required with the power supplies connected to the substrate and the thermionic emitter. The current limiter connected to the target supply is the most critical since it must handle the most power (50 kW for a unit designed for a commercial reprocessing facility or ~15 kW for a BRET^(a)-scale facility).

The control of arcs is believed to be important enough to test several approaches to the target power supply. The merit and status of the three approaches being considered are summarized in Table 6.1. Commercial power supplies with the desired control circuitry were not available when this program began; however, series tube current limiters developed for sputter deposition at PNL have been in use for over 10 years. The PNL current limiter uses a series triode as a fast-acting switch.

The first approach has been to design and test a circuit that would permit operating two or more of the PNL 2500-volt, 7-amp current limiters in parallel. The main advantage of this approach is derived from the high (80%) overall power supply/current limiter efficiency and the capability of reducing the voltage to near zero during fault conditions.

The second approach is similar to the first one except that three triodes operated in parallel are used to control the voltage of the power supply. This approach uses a commercial newly available power supply that was developed for a plasma-separation process. Experience with this unit indicates that it is probably the most rugged and reliable unit under consideration but has a

(a) Breeder Reprocessing Engineering Test.

TABLE 6.1. Merit and Status of Power Supply/
Current Limiter Approaches

Approach	Electrical Efficiency, %	Capital Cost, \$/kW	Status
1. PNL series-tube multi-limiter combination	~80	~0.50	Tested at 2200 V, 10 A
2. Commercial series-tube limiter	~60	~2.00	Delivery promised February 1984
3. Commercial solid-state shunt-type	~95	~0.70	Delivery promised January 1984

low electrical efficiency (60%) and a capital cost four times that of the PNL approach.

The third approach differs from the first two. Here the control circuitry senses the arc and the load is shunted through an active element placed in parallel with the load. This approach, proposed by a commercial power supply manufacturer, has two major advantages: high electrical efficiency (~95%) and low capital cost. A major concern with this method, however, is whether the voltage across the load drops enough to extinguish the arc during a fault condition.

To evaluate the three approaches, an arc simulation unit was designed and fabricated to test each power supply/current limiter combination before testing it on expensive gas-trapping runs. This procedure also makes it possible to analyze the results of the trapping tests independent of problems with the current limiter. The test system consists of a dummy resistive load that can dissipate the desired power when connected to the power supply/current limiter combination. A high-voltage relay rated at 15 kV, 50 amp is wired parallel to the dummy load and can be actuated on demand. The test equipment is mounted in a fan-cooled, standard 6-ft rack. The resistors can be easily connected in various ways, from a 4.5-kV, 8-amp load to a 1.5-kV 25-amp load with plans to increase the capacity to 2.5 kV, 25 amp.

Arcs can be simulated by activating the relay as often as every 100 milliseconds. A typical test condition is a 2-sec short-circuit in a 6-sec period. Automatic testing and data logging is facilitated by actuating the high-voltage relay with the computer control when the krypton-trapping unit is free. A two-tube PNL power supply/current limiter combination has been tested up to 50 hr at 2200 volts, 10 amps. This type of testing has revealed several defects, and their correction has led to improved reliability.

Characterization of Krypton-Containing Alloys

Environmental considerations dictate that krypton release be minimized in the storage of ^{85}Kr -containing deposits. It is also desirable that the release of ^{85}Kr be understood in the event of nonstandard conditions during storage or transportation. With these goals in mind, studies involving the release behavior of krypton in a sputter-deposited nickel-lanthanum alloy in oxygen at 320°C and at 290°C and in water at room temperature and at 90°C have continued. It was found that release behavior is related to the crystal-line state of the alloy. In addition, the expansion behavior of the Ni-La-Kr and Ni-Y-Kr alloys have been studied under both isothermal and linear temperature-increasing conditions. Expansion behavior is important

in final design considerations both in deposit formation and in long-term storage.

The release behavior of the Ni-La-Kr alloy was shown to be dependent on the crystalline state of the alloy. It is important for this report to review the kinetics of krypton release. The measured kinetics of krypton release from the alloy fits an activated diffusion rate law where spherical geometry is assumed and the fraction krypton released (F) at any given time (t) is (Barrer and Brook 1953; Barrer 1949; Crank 1975):

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp - \frac{Dn^2\pi^2 t}{r_o^2} \quad (1)$$

where

$$\frac{D}{r_o^2} = \frac{D_o}{r_o^2} \exp \frac{-E}{RT} \quad (2)$$

and D is the diffusion coefficient, r_o is the radius of a spherical diffusing unit, E is the activation energy for diffusion, R is the gas constant, and T is the temperature in degrees Kelvin. Equation (1) may also be written (Barrer and Brook; Crank):

$$F = 6 \left(\frac{Dt}{r_o^2} \right)^{1/2} \left[\frac{-1/2}{\pi} + 2 \sum_{n=1}^{\infty} \text{ierfc} \frac{n^2 r_o^2}{Dt} \right]^{1/2} - \frac{3Dt}{r_o^2} \quad (3)$$

where Equation (1) converges rapidly for large F and Equation (3) converges rapidly for small values of F . For small values of F , Equation (3) is approximated by (Barrer and Brook; Walker et al. 1966):

$$F = \frac{6}{\pi^{1/2}} \left(\frac{Dt}{r_o^2} \right)^{1/2} \quad (4)$$

Use of Equation (4) produces significant errors in the calculation by $F = 0.1$. However, by including the final term of Equation (3) so that

$$F = \frac{6}{\pi^{1/2}} \left(\frac{Dt}{r_o^2} \right)^{1/2} - \frac{3Dt}{r_o^2} \quad (5)$$

the errors are insignificant to $F = 0.87$ (Walker et al.).

Spherical geometry must be assumed even though the form of the deposit is a flat plate. This assumption is based on the apparent porosity of the material. The surface area of the alloy as measured by N_2 adsorption isotherms was nominally $100 \text{ cm}^2/\text{g}$. The density was 7.2 g/cm^3 , which would lead to the same surface area if the alloy was in the form of spherical particles of $80 \text{ }\mu\text{m}$ dia. Thus we have concluded that the material is a porous structure such that diffusing cells are bounded by pores with access to the surface. Therefore krypton needs only to diffuse from a cell to a pore to be released. Although the shapes of the diffusing cells probably deviate from spherical and are not of uniform size, similar cases have previously shown that the assumption of a spherical geometry is justified (Barrer and Brook; Walker et al.).

Equations (1 through 5) were used to calculate the diffusion coefficient from krypton release data. Equation (3) was used for values of F smaller than 0.1 for both isothermal and nonisothermal krypton release. For isothermal release, a plot of F^2 versus t yields a straight line with a slope (S) equal to:

$$S = \frac{36}{\pi} \frac{D}{r_o^2} \quad (6)$$

and intercept zero. For nonisothermal release, a plot of F^2 versus t yields a

monotonically increasing curve. The data indicate that the slope of the curve at any given time or temperature is about equal to Equation (6) for the nonisothermal case. Thus nonisothermal data can be used to evaluate the diffusion coefficient. For values of F greater than 0.1 during isothermal release, values for $(D/r_0^2)^{1/2}$ were evaluated by trial and error using Equations (1) and (5).

The Arrhenius plots of four release tests (two isothermal and two nonisothermal) are shown in Figure 6.1. The activation energy for krypton release was nearly a factor of five less for nonisothermal release than for

isothermal release at temperatures below 400°C. The activation energy was about the same for the two cases at temperatures above 400°C. The variation in release behavior between the isothermal and nonisothermal cases was correlated with a transition in the crystalline state of the alloy.

Two transitions are indicated by the differential scanning calorimeter curve of Figure 6.2. The first transition corresponded to the temperature at which the values for isothermal and nonisothermal diffusion coefficients converge (see Figures 6.1 and 6.2). The second transition, shown in Figure 6.2, corresponded to the temperature at which

FIGURE 6.1. Activation Energy Plot for the Release of Krypton from a $\text{Ni}_{0.81}\text{La}_{0.09}\text{Kr}_{0.10}$ Alloy Based on Both Isothermal and Nonisothermal Data

FIGURE 6.2. Analysis of a Differential Scanning Calorimeter Curve Showing Two Exothermic Transitions of the $\text{Ni}_{0.81}\text{La}_{0.09}\text{Kr}_{0.10}$ Alloy at a Heating Rate of $20^\circ\text{C}/\text{min}$

rapid release of krypton occurred (compare Figures 6.2 and 6.3). The thermal changes during that transition were more erratic because of autocommunication of the alloy due to stresses built up during krypton release.

Crystallographic x-ray diffraction data of the Ni-La-Kr alloy, after heat treatment for 45 min at various temperatures, also show two crystalline transitions (Knoll and McClanahan 1983). The first is from an amorphous state to a body center cubic (bcc) state beginning appreciably between 300°C and 350°C , and becoming complete by 425°C even at rapid heating rates; the second is from the bcc state to a hexagonal state occurring appreciably at 550°C and becoming complete by 650°C .

FIGURE 6.3. Thermal Gravimetric Analysis Showing Weight Loss Due to Krypton Release from the $\text{Ni}_{0.81}\text{La}_{0.09}\text{Kr}_{0.10}$ Alloy at a Heating Rate of $20^\circ\text{C}/\text{min}$

The overall kinetics of the first transition, which consisted of a combination of nickel and nickel-lanthanum crystallite formation, has been evaluated from nonisothermal data with a constant temperature increase of $4^\circ\text{C}/\text{min}$. The data fit an activated diffusion rate law and the kinetic factors were evaluated using Equations (2) and (6). The results are shown in Table 6.2. These results can only be considered approximate for predicting the extent of crystallization within a given time. Inaccuracies can be attributed to uncertainties in baseline determination, the formation of two crystallites (nickel and nickel-lanthanum) in the same temperature range, and the use of nonisothermal data to predict isothermal results. Data on the kinetics of crystallization are presented to emphasize that after this alloy has been held at temperatures above 200°C for long periods of time, extensive crystallization can occur. Thus, under isothermal conditions where krypton release data were taken over long periods of time at temperatures below 400°C , the alloy became crystalline and the release rate dropped to what would be expected for a crystalline material. Under nonisothermal conditions, however, the alloy attained a

TABLE 6.2. Estimated Fraction Crystallized to a bcc Structure at Various Times and Temperatures for a $\text{Ni}_{0.81}\text{La}_{0.09}\text{Kr}_{0.10}$ Alloy, Based on Nonisothermal ($4^\circ\text{C}/\text{min}$ temperature increase rate) Differential Scanning Calorimeter Data. $E = 40 \text{ kcal/mole } D_0/r_0^2 = 6.3 \times 10^{-10}$.

Temp, $^\circ\text{C}$	Yr at Temp		
	1	5	10
25	4.0×10^{-7}	9.0×10^{-7}	1.2×10^{-6}
90	3.1×10^{-4}	7.0×10^{-4}	9.8×10^{-4}
150	0.024	0.053	0.074
200	0.32	0.62	0.79

much higher temperature before extensive crystallization occurred. The krypton release rate was then the same as would be expected from an amorphous material until about 400°C when the crystalline transition became very rapid.

These crystallographic/krypton-release data suggest several advantages of this alloy as a storage medium including the following:

1. During sputter deposition, krypton is incorporated into a metal or metal alloy in greater quantities and with less cost if the material is in its amorphous, rather than crystalline, state (Tingey et al. 1979).
2. During storage, krypton is retained more tenaciously in the Ni-La-Kr alloy at temperatures below 400°C if the alloy is in its bcc crystalline state rather than its amorphous state.
3. The alloy can be transformed from the amorphous state to the bcc crystalline state with negligible loss of krypton. Thus the Ni-La-Kr alloy can be deposited in the amorphous state with less cost and stored in the bcc crystalline state, providing an ideal and safe storage medium for radioactive ^{85}Kr .

4. Another advantage is the alloys' resistance to oxidation. The oxidation tests of samples both in water and in oxygen have continued for more than a year. These results are reviewed and compared to release in vacuum in Table 6.3. It appears that under any anticipated storage conditions the Ni-La-Kr alloy will not release substantial quantities of ^{85}Kr .

The thermal expansion behavior of krypton-containing alloys has been recognized as an important factor of deposition. Some alloys can contract after deposition. Contraction would not cause any problems during storage, but during deposition contraction can cause cracking and debonding of the deposit from the substrate. If pieces of the deposit spall off, they can short filament electrodes and cause premature shutdown. Figures 6.4 and 6.5 show the thermal expansion curves for a Ni-Y-Kr and a Ni-La-Kr alloy, respectively. The Ni-Y-Kr alloy never goes through a period of contraction; however, during the first heating it expands more slowly from about 150 to 220°C. Conversely, the Ni-La-Kr alloy contracts from 120 to 270°C (the linear dimension decreasing by more than 0.25%). Thick deposit experiments on these two alloys have

TABLE 6.3. Extrapolated Total Fraction Krypton Release in 10 Yr for the $\text{Ni}_{0.81}\text{La}_{0.09}\text{Kr}_{0.10}$ Alloy at Various Conditions

Temp, °C	Material State and Conditions			
	Amorphous in Vacuum	Crystalline in Vacuum	Amorphous in Water	Crystalline in Oxygen
25	1.12×10^{-4}	6.63×10^{-18}	1.5×10^{-2}	
90	1.46×10^{-3}	1.02×10^{-12}	3.52×10^{-2}	
150	7.77×10^{-3}	2.42×10^{-9}		
200	(a)	3.47×10^{-7}		
300	(a)	5.32×10^{-4}		$1.42 \times 10^{-4}(b)$

(a) Alloy crystallizes extensively during the 10-yr period (see Table 6.2).

(b) Extrapolated from data at 320°C.

FIGURE 6.4. Expansion Versus Temperature for $\text{Ni}_{0.82}\text{Y}_{0.11}\text{Kr}_{0.07}$ Heated at $20^\circ\text{C}/\text{min}$

FIGURE 6.5. Expansion Versus Temperature for $\text{Ni}_{0.81}\text{La}_{0.09}\text{Kr}_{0.10}$ Heated at $20^\circ\text{C}/\text{min}$

indicated a problem of debonding and spallation with the Ni-La-Kr alloy, but no such problem was experienced with the Ni-Y-Kr alloy, even to a deposit thickness of over 6 millimeters. Further experiments and characterization are planned to define conditions for sputtering thick deposits of Ni-La-Kr without spallation.

The Ni-Y-Kr sample was tested for time-dependent expansion under isothermal conditions at 304°C . As seen in Figure 6.6, the sample expanded a small amount during the first few days, but after 5 days expansion leveled off. Based on these data, the isothermal expansion will cause no difficulty during storage. Further testing will be done to confirm this conclusion.

FIGURE 6.6. Isothermal Expansion Versus Time for Ni-Y-Kr Held at 304°C

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